STRUCTUROCHEMICAL STUDIES OF SOME SCHIFF BASE COMPLEXES OF THE FIRST ROW TRANSITION METAL ELEMENTS

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COMPLEXES OF THE FIRST ROW TRANSITION METAL ELEMENTS

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SUMMARY

PART I

COMPLEXES WITH THE DIIMINE OF 2,4-PENTANEDIONE AND 2-AMINOETHANOL

Preparations are reported for a series of five transition metal complexes containing the diimine ligand of 2,4-pentanedione and 2-aminoethanol. On the basis of chemical analyses, magnetism and x-ray diffraction studies, these complexes have been formulated as: Co(DIIMINE)$(ETAH)_2$, $[Ni(H\cdot DIIMINE)]_2$, $[Cu(H\cdot DIIMINE)]_2$, $Ni_3(DIIMINE)_2(ETAH)_4$, and $Ni_2(DIIMINE)(OH)$; where DIIMINE and H·DIIMINE represent the tri- and divalent tetradentate diimine ligand respectively, and ETAH represents neutral 2-aminoethanol.

The first three complexes were the subjects of x-ray structure determinations. The molecular structure of the cobalt complex consists of a cobalt(III) ion coordinated to a planar, tetradentate diimine ligand, $(DIIMINE)^{3-}$, and two monodentate 2-aminoethanol groups, (ETAH). The coordination geometry shows only small deviations from an ideal octahedral geometry. Extensive hydrogen bonding, involving the 2-aminoethanol hydroxide groups and the donor oxygen atoms of the diimine ligand, results in an infinite chain pattern in the solid state.

The nickel and copper complexes with the formula, $[M(H\cdot DIIMINE)]_2$, were shown to be isomorphous and isostructural. They consist of a divalent metal ion, M, coordinated by a planar bivalent tetradentate lig-

and, $(H\cdot DIIMINE)^{2-}$, with a square-planar arrangement of donor atoms. The remaining proton on each metal unit, M(H·DIIMINE), participates in strong intermolecular hydrogen bonding with a second metal unit, creating individual hydrogen bonded dimeric units of the formula, $[M(H\cdot DIIMINE)]_2$. The dimeric units, which are relatively undissociated in freshly prepared chloroform solutions, have exceedingly short hydrogen-bonded oxygen-oxygen contacts of 2.28-2.31Å. These contacts are the shortest ever reported between hydrogen-bonded oxygen atoms. The hydrogen bonded dimeric copper complex exhibits antiferromagnetism as evidenced by the magnetic moments: $\mu_{eff}^{298^\circ K} = 1.69(1)$ B.M., $\mu_{eff}^{193^\circ K} = 1.56(2)$ B.M., and $\mu_{eff}^{77^\circ K} = 1.14(4)$ B.M. The antiferromagnetism is the result of superexchange via a σ-pathway involving the hydrogen bridge.

Reasonable molecular structures are presented for the two complexes that were not the subjects of x-ray structure determinations. The proposed structures are based upon the known magnetism of these complexes as compared to the magnetism of other complexes believed to be structurally similar to them.

PART II

COMPLEXES WITH THE IMINE OF SALICYLALDEHYDE AND GLYCINE

The structure and magnetic properties are reported for some iron, cobalt and manganese complexes containing the Schiff base of salicylaldehyde and glycine. The magnetic moments of these compounds are consistent with the observed structures and formulation, $[M(II)(H_2O)_6]\cdot[M(III)(SALGLY)_2]\cdot 2H_2O$ (where M(II) and M(III) refer to a metal in the +2 and +3 oxidation states, respectively, and SALGLY represents the

the divalent tridentate imine ligand of salicylaldehyde and glycine). The divalent metal ions are octahedrally coordinated by six water molecules. The trivalent metal ions are octahedrally coordinated by two $(SALGLY)^{2-}$ ligands such that the two oxygen atoms in each tricoordinated ligand unit are trans to one another, thereby allowing the metal(III) ion and the O_2N donor atoms of each ligand to be coplanar. These ionic complexes are held together by hydrogen bonding and exhibit no apparent magnetic interactions between metal ions. In the cases where the metal is either iron or manganese, the effect of hydrogen bonding between coordinated metal ions is to create infinite chains of complex ions in the solid state. The cobalt compound is somewhat different, however, in that the hydrogen bonding creates individual trimeric units. These complexes are structurally related to the pyridoxal-phosphate Schiff base complexes, and thus may be helpful in elucidating the role of mixed-oxidation state complexes in the biologically relevant pyridoxal-phosphate-dependent amine oxidase reaction.

PART I

COMPLEXES WITH THE DIIMINE OF

2,4-PENTANEDIONE AND 2-AMINOETHANOL

CHAPTER I

INTRODUCTION

From the sheer magnitude of the relevant chemical literature on the subject of magnetic exchange, there is little doubt that this subject has aroused the interest of inorganic chemists. Interest in magnetic exchange developed in 1951 when it was observed that copper(II) acetate monohydrate exhibited a subnormal room temperature magnetic moment of 1.43 B.M. and an antiferromagnetic variation of susceptibility with temperature (1,2). More recently a large number of additional copper(II) compounds which have subnormal moments at room temperature have been reported; they are reviewed in an excellent article by Kato, Jonassen and Fanning (3).

"Magnetic exchange" refers to a whole variety of magnetic interactions that may take place between paramagnetic atoms, and in most instances conditions dictate which types of exchange will dominate the magnetism. Because of the relevancy of these exchange mechanisms to the examples which follow, the reader may find several reviews quite helpful (4-6). Particular emphasis will be placed on the "superexchange mechanism" as applied to the interaction between d^9 metal ions which will be the only cases discussed. A complete mathematical explanation of the magnetic behavior of these examples is beyond the capabilities of this author and the scope of this work; consequently, only qualitative descriptions will be given. Once enough background on the subject of exchange coupling in copper(II) compounds is covered, the reader will be

introduced to a new copper(II) complex that has a novel hydrogen-bonded dimeric structure and exhibits exchange coupling through a hydrogen bridge. In addition, mention will be made of a whole series of complexes involving a variety of metal ions which are both structurally and chemically related to the copper complex.

Probably the most important prerequisite for understanding the magnetic behavior of a complex is its molecular structure. This is especially true when the magnetic susceptibility data do not fit the theoretical curve for the behavior of isolated magnetic atoms (c.f. the Curie-Weiss law, 7-8). Deviations from Curie-Weiss law dependence generally occur when the metal ions aggregate into clusters, each cluster of metal ions being insulated from every other cluster by organic ligands. In such cases, magnetic interactions between metal ions within each cluster will dominate the magnetic properties of the material. Only at very low temperatures ($\sim 20^{\circ}K$) will interclusteral interactions appear, and even then, the effect may not be large. Within a given cluster, factors such as the metal-metal separation; the electronic configuration of the metal, the anions and the ligands; and, the molecular symmetry of the cluster play a part in determining the overall magnetic behavior of the cluster.

Generally, it is found that the overall magnetic behavior of a cluster of metal ions will be either ferromagnetic or antiferromagnetic. For both types of behavior the magnetic susceptibility, χ, will show the Curie or Curie-Weiss law dependence at high enough temperatures. However, when the temperature is lowered through a characteristic temperature, the Curie point, substances with ferromagnetic behavior will show

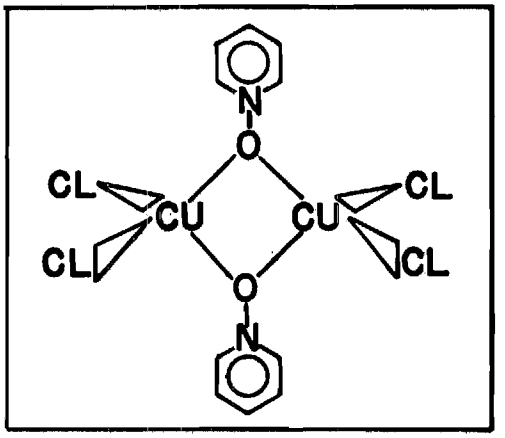
a greater susceptibility than predicted by the Curie-Weiss law. For antiferromagnetic behavior, just the opposite is observed; namely, as the temperature drops below the characteristic temperature, in this case the Neel point, the susceptibility becomes less than predicted by the Curie-Weiss law. In some compounds, these effects are due to lattice (intermolecular) interactions but in other compounds, these effects are due to interactions within discrete units (intramolecular).

When dealing with the first row transition metal elements, these magnetic interactions usually are explained in terms of spin contributions only, ignoring orbital contributions as being zero or very small. The result is that only spin-coupling mechanisms need be considered for explaining the magnetic behavior of the cluster. In most cases, one or more coupling constants, J, are required to describe the spin-spin interactions. A series of relevant examples will follow, showing the kinds of magnetic behavior associated with a number of structural arrangements of copper atoms.

By far the most extensively studied structural grouping of copper ions has been the oxygen-bridged binuclear complexes (3). A typical example of a μ_2-oxygen-bridged copper dimer is the complex drawn in (1), $[Cu(\text{pyridine-N-oxide})Cl_2]_2$. The pathway for magnetic interactions between copper ions in these complexes is believed to proceed via the bridging oxygen atoms employing the superexchange mechanism.

In first presenting his theory on the superexchange mechanism, Kramers (9) proposed that exchange coupling between magnetic centers could proceed through intervening diamagnetic ions by mixing into the ground state small amounts of excited states in which the intervening ions

have unpaired spins arising from electron transfer to the metal ions.



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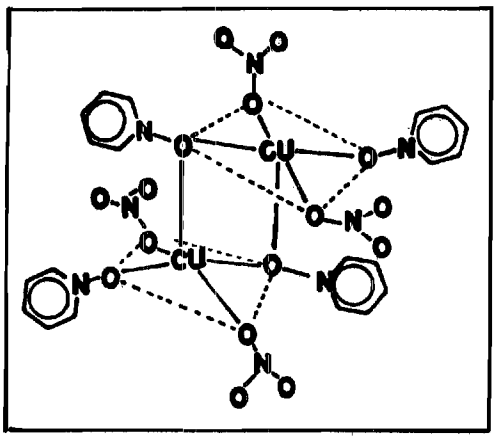
Kramers' theory has been expanded (10-12) and relationships between the sign of the exchange integral and the symmetry properties of the orbitals on the intervening ions have been derived (13-15). These relationships are often referred to as the Goodenough-Kanamori rules. Ginsberg (6) has used these rules to predict the magnetic behavior for a number of geometrical configurations of metal ions. In short, if the unpaired spin on the intervening ion resides in an orbital that is non-orthogonal to orbitals on the metal containing unpaired spins, then antiferromagnetic coupling ($J<0$) is expected. This interaction has been referred to by some authors as "incipient chemical bonding" (3,4). On the other hand, if the orbitals in question are orthogonal, ferromagnetic coupling ($J>0$) is expected. Most of the μ_2-oxygen complexes of copper(II) having Cu-Cu separations between 2.8 and 3.3 Å show strong antiferromagnetic coupling at room temperature. Compounds such as $[Cu(\text{pyridine-N-oxide})Cl_2]_2$ (16), $[Cu(PIA)]_2$ (17), $[Cu(SALPAH)Cl]_2$ (18), and $[Cu(C_8H_{10}N_2O)]_2$ (19) exhibit such behavior. Structural and magnetic data, as well as ligand code identifications for these compounds and all the others to be referred to

later can be found in Table 1.

Often times, interest in a complex has been diminished somewhat and a structure determination of the complex not attempted when a "normal" room temperature moment (i.e. close to the spin-only value for a reasonable coordination geometry of the metal) has been observed. However, it is possible to have magnetic coupling at lower temperatures even though spin-spin coupling is not observed at room temperature and such compounds may be abstrusely deceiving if their magnetic susceptibility is not determined at several temperatures. Recently, it has been observed that a number of so-called "out-of-plane" dimers (20a), such as the oxygen bridged complexes $[Cu(pyridine\text{-}N\text{-}oxide)(NO_3)_2]_2$ (21), $[Cu(tyr)_2]_2$ (22), $[Cu(dmg)_2]_2$ (23), and the sulfur-bridged complex $[Cu(edtc)_2]_2$ (24), show significant ferromagnetic coupling at low temperatures, thus suggesting a triplet ground state for the copper atoms (see Table 1). A typical "out-of-plane" dimer is drawn in (2). Inman, Hatfield and Drake (25) have



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studied the structure and magnetic behavior of the β-form of $[Cu(8\text{-}hqn)_2]_2$ and have shown that significant ferromagnetic spin-spin interactions in the parallel "out-of-plane" oxygen-bridged dimer could not be observed

Table 1. Summary of the Structures and Magnetic Properties of Some Copper Complexes

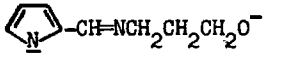
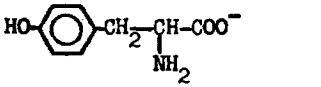
Compound Identification	[a]Notes on Structure	[b]Coordination of Copper	Magnetic Moment (B.M.)	Temperature Range (°K)	[c]Magnetic Behavior	Reference Numbers
$[Cu(Pyridine\text{-}N\text{-}Oxide)Cl_2]_2$	Dimer; μ_2-oxy	Tetrahedral	0.85	298	[d]Anti-F	16
$[Cu(PIA)]_2$; PIA=dianion of 2-(3-hydroxypropylimino)pentanone-4 = $^-OC(CH_3)=CHC(CH_3)=N-CH_2CH_2CH_2O^-$	Dimer; μ_2-oxy Cu-Cu=3.03Å	Sqr. Planar	0.41	298	Anti-F	17
$[Cu(SALPAH)Cl]_2$; SALPAH=monoanion of N-(3-hydroxypropyl)salicylaldimine= $^-OC_6H_4CH=N(CH_2)_3OH$	Dimer; μ_2-oxy Cu-Cu=3.29Å	Trig. Bipy.	1.10	298	Anti-F	18
$[Cu(C_8H_{10}N_2O)]_2$; $C_8H_{10}N_2O$= dianion of N-(3-hydroxypropyl)-pyrrole-2-carboxaldimine= 	Dimer; μ_2-oxy Cu-Cu=3.00Å	Sqr. Planar	0.54	298	Anti-F	19
$[Cu(Pyridine\text{-}N\text{-}Oxide)_2(NO_3)_2]_2$	Dimer; Out-of-Plane Oxy-Brdg.	Tet. Pyr.	1.90[e]	2.40-300	F $J= +10\ cm^{-1}$	21,26
$[Cu(tyr)_2]_2$; tyr=tyrosinate 	Dimer; Out-of-Plane Oxy-Brdg. Cu-O=2.43Å[f]	Tet. Pyr.	1.84[g]	2.50-300	F $J= +9.5\ cm^{-1}$	22,27

Table 1. (Continued)

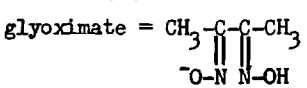
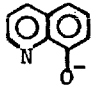
$[Cu(dmg)_2]_2$; dmg=1,2-dimethylglyoximate = 	Dimer; Out-of-Plane oxy-Brdg. Cu-O=2.43Å[f]	Tet. Pyr.	2.00-2.05[h]	4.20-55	F J= +14.9 cm^{-1}	23,28
$[Cu(edtc)_2]_2$; edtc=N,N-diethyldithiocarbamate = $(C_2H_5)_2N-CS_2^-$	Dimer; Out-of-Plane S-Brdg. Cu-S=2.85Å[i]	Tet. Pyr.	1.85-1.90[j]	4.20-56	F J= +12.0 cm^{-1}	24
$[Cu(8\text{-hqn})_2]_2$; 8-hqn=8-hydroxyquinolinate = 	Dimer; Out-of-Plane Oxy-Brdg. Cu-O=2.83Å[f]	Tet. Pyr.	1.82-1.90[k]	3.20-77	P	25,30 31,32
Acetylacetone-mono(o-hydroxyanil) copper(II); ligand= $^-OC_6H_4N{=}C-(CH_3)CH{=}C(CH_3)O^-$	Tetramer Two Displaced Dimers	Tet. Pyr.	1.37 (298°K)	90-400	C[l]	36,37
$[Cu(EIA)]_4$; EIA=dianion of N-(2-hydroxyethylimino)pentanone-4= $^-OC(CH_3){=}CHC(CH_3){=}NCH_2CH_2O^-$	Tetramer "Cubane"	Trig. Bipy.	1.87 (298°K)	1.5-300	C[m]	6,17
$Cu_4OCl_6(TPPO)_4$; TPPO=triphenylphosphineoxide= $(C_6H_5)_3P-O$	Tetramer μ_4-oxo	Trig. Bipy	1.93 (294°K)	1.63-294	C Isotropic J= +40°K	39,41

Table 1. (Continued)

$[Cu_4OCl_{10}][N(CH_3)_4]_4$	Tetramer μ_4-oxo	Trig. Bipy.	1.69 (294°K)	1.54-294	Anti-F J= -16 cm^{-1}	39-42
$[Cu(H\cdot DIIMINE)]_2$; H·DIIMINE= dianion of N,N'-bis(2-hydroxy-ethyl)-2,4-pentanediimine	Dimer; Hydrogen bonded	Sqr. Planar	1.69 1.56 1.14	297 193 77	Anti-F	this work

[a] μ_2-oxy=μ_2-bridging oxygen; Out-of-Plane Oxy-Brdg.=μ_2-oxygen bridging out of the coordination planes of the copper atoms; Out-of-Plane S-Brdg.=μ_2-sulfur bridging out of the coordination planes of the copper atoms.

[b] Sqr. Planar=Square Planar; Trig. Bipy.=Trigonal Bipyramidal; Tet. Pyr.=Tetragonal Pyramidal

[c] Anti-F=Antiferromagnetic; F=Ferromagnetic; P=Normally Paramagnetic; C=Complex Magnetic Behavior

[d] $J = -650\ cm^{-1}$

[e] Fitted to Curie-Weiss law with $\theta = +2°K$ and $C = 0.449$ emu-deg-m^{-1}

[f] Copper to out-of-plane oxygen distance

[g] Fitted to Curie-Weiss law with $\theta = -5°K$ and $C = 0.411$ emu-deg-m^{-1}

[h] Fitted to modified Langevin equation with $\theta = -1.45°K$; Modified Langevin equation: $\chi = \frac{Ng^2\beta^2}{3k(T-\theta)}\left(1 + \frac{1}{3}\exp(-2J/kT)\right)^{-1}$

[i] Copper to out-of-plane sulfur distance

[j] Fitted to modified Langevin equation with $\theta = -1.37°K$

[k] Fitted to Curie-Weiss law with $\theta = 0°K$ in the temperature range 8.1-200°K

[l] $J_{13} = -140$; $J_{12} = -48$; $J_{14} = +134$; and $J_{34} = 0\ cm^{-1}$

[m] $J_L = +4$ and $J_S = -15\ cm^{-1}$

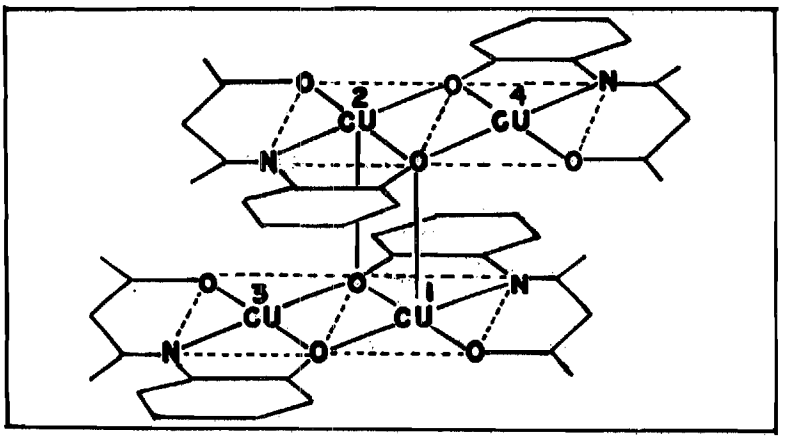
because the "out-of-plane" copper-oxygen distances were greater than 2.8Å.

Although "out-of-plane" bridged, bimetallic copper complexes usually possess a triplet ground state (i.e. exhibit intradimer ferromagnetism) (20b), two interesting exceptions to this rule are the "out-of-plane" halogen-bridged dimers, dichloro- and dibromo-(2-methylpyridine)copper(II) complexes (33-35). The authors attribute the antiferromagnetic behavior of these complexes to the fact that both chlorine and bromine have low lying d-orbitals capable of σ-overlap with the d-orbitals on copper, thus providing the non-orthogonal pathway necessary for antiferromagnetic exchange. Clearly, these two examples illustrate quite vividly the need to consider the electronic characteristics of the bridging atom and the role it plays in determining the overall magnetic behavior of a metal cluster.

So far we have considered only dimeric copper complexes whose magnetic behavior could be described in terms of a single coupling constant. Clearly, as the number of copper ions in a cluster goes up, so also does the number of coupling constants. Generally, coupling constants between symmetry equivalent copper atoms will be equal, so the actual number of coupling constants will be symmetry dependent. The following cases will serve to exemplify the magnetic behavior of copper clusters described by more than one coupling constant.

The simplest type of cluster observed for copper(II) compounds after the dimer is the tetramer. Probably the most exhaustively studied copper tetramer has been the complex, acetylacetone-mono-(o-hydroxyanil) copper(II). When the x-ray structure of this compound was reported in 1961 (36a), the structure was described as containing dimeric units. In

fact, the magnetic behavior was purported to obey the Bleaney-Bowers equation[1] for a typical μ_2-oxygen-bridged exchange coupled copper dimer. A closer examination of the structure (36b) reveals its tetrameric nature. The structure can be thought of as having been formed by displacing two dimers as shown in (3). Hatfield (37) has examined the magnetic suscep-



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tibility of this compound over the temperature range, 96-400°K, and has shown that deviations in the susceptibility occurred which were not predicted from the equation for exchange coupled dimers, and that these deviations could be corrected by using the Hamiltonian appropriate for a tetramer. The problem was similar in details to the A_2X_2 problem in high-resolution nuclear magnetic resonance (38). Four coupling constants were determined, J_{13}= -140, J_{12}= -48, J_{14}= +134 and J_{34} = 0 cm^{-1}. Their

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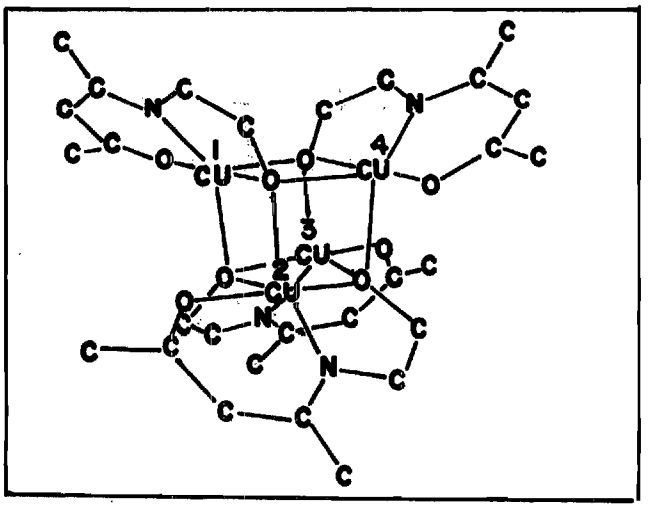
[1]Bleaney-Bowers equation: $\chi = (g^2N\beta^2/3kT)(1 + \frac{1}{3}\exp(-J/kT))^{-1} + N\alpha$

χ = susceptibility per gram atom of copper
J = exchange integral (equal to the singlet-triplet splitting)
g = magnetic field splitting factor
$N\alpha$ = temperature independent paramagnetism (correction term)
k = Boltzmann's constant
T = absolute temperature
β = Bohr magneton
N = Avagadro's number

signs and magnitudes are consistent with the postulate that antiferromagnetic superexchange occurs between adjacent pairs of copper ions, 1-3, 2-4, and 1-2, while ferromagnetic superexchange occurs between copper ions 1-4 and 2-3. Thus it is possible to have both ferromagnetic and antiferromagnetic exchange coupling in a single cluster.

Another type of copper cluster that shows exchange coupling is the so-called "cubane" complex (17), $[Cu(EIA)]_4$, in which copper and oxygen atoms occupy alternate corners of a rather distorted cube (4). Like the



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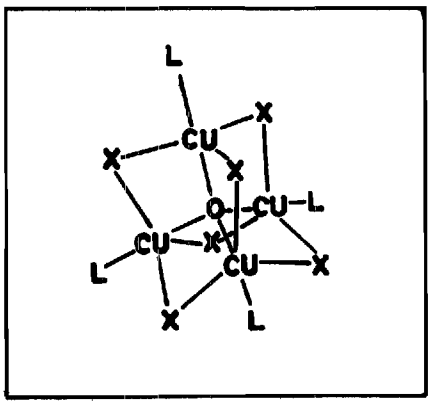
previous example, it also has both ferromagnetic and antiferromagnetic exchange integrals appearing in the expression for the Hamiltonian, but unlike the previous example, the exchange effects are observed at much lower temperatures. Since the center of the cubane sits on a fourfold inversion axis, many of the coupling integrals become equal; $J_{12}=J_{13}=J_{24}=J_L$ and $J_{14}=J_{23}=J_S$; thus simplifying the calculations somewhat. By fitting the susceptibility versus temperature (1.5-300°K) data for the copper tetramer to the theoretical susceptibility equation, the coupling constants were found to be: $J_L= +4\ cm^{-1}$ and $J_S= -15\ cm^{-1}$ (6).

Finally, there are the μ_4-oxo complexes $Cu_4OX_6L_4$ (X=Cl, L=O of $(C_6H_5)_3PO$; X=Br, L=O of $(C_6H_5)_3PO$; and X=Br, L=N of C_5H_5N) which show an unusual type of exchange mechanism, called antisymmetric vector coupling. Antisymmetric vector coupling (39) occurs in these complexes because the ground state for the copper atoms in the cluster is orbitally degenerate, or nearly so. Significant spin-orbit coupling occurs and isotropic exchange alone cannot adequately account for the magnetic behavior. Up till now, the complexes discussed possessed orbitally singlet single-ion ground terms; consequently, spin-spin interactions dominated the magnetic behavior. The μ_4-oxo complexes, however, are the first examples of metal clusters which do not follow the general trend.[2] A typical μ_4-oxo complex is drawn in (5). Surprisingly enough, the structurally similar



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μ_4-oxo anionic cluster, $[Cu_4OCl_{10}]^{4-}$, shows only isotropic coupling in the temperature range 4.2-295°K (40,42). The cluster shows antiferromagnetic behavior with a Neel temperature of about 29°K and a coupling constant, J, of -16 cm^{-1} (all four copper atoms are symmetry equivalent). At the

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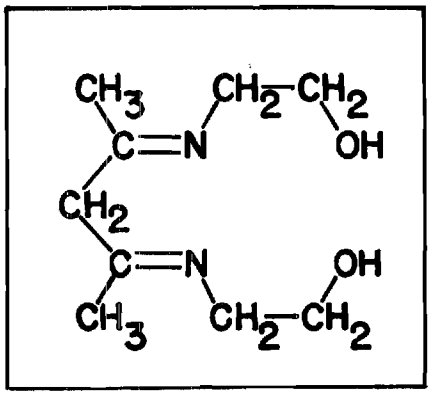
[2]Ginsberg postulates (6) that another complex likely to possess an orbitally degenerate ground state for the metal ions is the "cubane" complex, tetrakis-[μ_3-methoxo-2,4-pentanedionatomethanol cobalt(II)](43).

present time there is uncertainty as to why the copper ions in the structurally similar clusters $Cu_4OX_6L_4$ and $[Cu_4OCl_{10}]^{4-}$ have different ground term orbital multiplicities.

So far this work has touched upon a number of structural arrangements of copper atoms which show interesting magnetic properties. We have mentioned complexes containing monatomic oxygen, sulfur and halogen bridges, in-plane and out-of-plane μ_2-oxygen-bridged dimers, displaced dimers (i.e. tetramers), cubanes and μ_4-oxo-bridged clusters. In the hope of preparing further examples of oxygen-bridged cluster compounds with interesting magnetic properties (c.f. $[Cu(EIA)]_4$ and $[Cu(PIA)]_2$), an attempt was made to prepare complexes of N,N'-bis(2-hydroxyethyl)-2,4-pentanediimine (i.e. the diimine formed from 2,4-pentanedione and 2-aminoethanol).[3] This ligand (6) will be abbreviated as H_3DIIMINE.



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Complexes containing diimines of 2,4-pentanedione are still fairly rare. Some successful preparations have been achieved by using the

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[3] A compound of this kind, made by reacting an aldehyde or ketone with a primary amine, and containing the azomethine group, $>C=\dot{N}-R$, is called a Schiff base. The Schiff base so formed can then coordinated to metal ions through the electron pair on the nitrogen atom.

preformed ligand (44,47) and only complexes of the macrocyclic ligand formed from 2,4-pentanedione and diethylenetriamine have been prepared directly (45,46) by "template reactions".[4] Since the latter method was the more direct approach, complexes of (6) were successfully prepared by template reactions. Since the potentially tetradentate ligand H_3DIIMINE contains three ionizable protons, it is possible for a trivalent metal ion to form neutral complexes M(DIIMINE) and for a divalent metal ion to form anionic mononuclear complexes $[M(DIIMINE)]^-$, neutral trinuclear complexes $M_3(DIIMINE)_2$, or neutral protonated complexes M(H·DIIMINE). By using different metal ions and varying the reaction conditions somewhat, it was possible to isolate a trinuclear nickel(II) complex, $Ni_3(DIIMINE)_2(ETAH)_4$ (where ETAH represents neutral 2-aminoethanol); a dinuclear nickel(II) complex of formulation, $Ni_2(DIIMINE)(OH)$; dinuclear copper(II) and nickel(II) complexes of formulation, $[M(H\cdot DIIMINE)]_2$, and a mononuclear cobalt(III) complex, $Co(DIIMINE)(ETAH)_2$. Since all of these complexes contain both alcohol and alkoxide groups, unusual types of hydrogen bonding were possible. Intermolecular hydrogen bonding creating an infinite chain pattern was observed for the cobalt(III) complex, while both the nickel(II) and copper(II) complexes, $[M(H\cdot DIIMINE)]_2$, participated in "cooperative" hydrogen bonding as in the mixed cobalt(III)--nickel(II) complex of 2-aminoethanol (48). The "cooperative" hydrogen bonding in the copper(II) complex was strong enough to give rise to antiferromagnetic exchange between the copper ions. This is the first

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[4] A template reaction is one that would not otherwise take place without the orienting effect of a metal ion in the process of complexing with the reaction products.

reported instance of the transfer of magnetic exchange across a hydrogen bridge. Consequently, this work reports the preparation, structure and magnetic properties of the mononuclear cobalt(III) complex, the dinuclear copper(II) and nickel(II) complexes, $[M(H\cdot DIIMINE)]_2$, and the preparation of the trinuclear nickel(II) complex. The preparation of a second dinuclear nickel(II) complex of formulation, $Ni_2(DIIMINE)(OH)$, is also reported.

CHAPTER II

EXPERIMENTAL

Preparation of Complexes[1]

Cobalt(III) Complex of N,N'-Bis(2-Hydroxyethyl)-2,4-Pentanediimine, Co(DIIMINE)$(ETAH)_2$

To a solution of 25 ml. of acetylacetone, $(CH_3CO)_2CH_2$, and 50 ml. of 2-aminoethanol, $HOCH_2CH_2NH_2$, was added cobalt(II or III) acetylacetone (0.01 mole) and potassium hydroxide (0.01 mole). The resulting slurry was heated gently to 115°C until everything had dissolved and most of the waters of condensation had been driven off. The solution was stoppered and set aside for crystallization. After twenty-four hours, the dark red crystals which had formed were collected by filtration through a Buchner funnel and washed several times with n-butanol. The crystals were examined under a polarizing microscope and found to be dichroic. They are subject to slow hydrolysis in air and must be dried in a vacuum at 100°C. After drying, they may be kept indefinitely without decomposition in a well-stoppered bottle. The crystals obtained in this manner were large enough for x-ray work. Elemental analysis of the product gave the following results.

Anal. Calcd. for $CoC_{13}H_{29}N_4O_4$: C, 42.85; H, 8.02; N, 15.37

Found: C, 42.92; H, 7.82; N, 15.38

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[1] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee and Atlantic Microlabs, Atlanta, Georgia.

Dimeric Nickel(II) and Copper(II) Complexes of N,N'-Bis(2-Hydroxyethyl)-2,4-Pentanediimine, $[M(H\cdot DIIMINE)]_2$

To a solution of 25 ml. of acetylacetone, $(CH_3CO)_2CH_2$, and 50 ml. of 2-aminoethanol, $HOCH_2CH_2NH_2$, was added the appropriate divalent metal acetylacetonate complex (0.01 mole) and potassium hydroxide (0.01 mole). This mixture was heated gently to 115°C and stirred until a green precipitate began to form on the sides of the flask. Heating was stopped immediately and the mixture set aside for crystallization. After sitting for approximately one week, the mixture yielded a green product which was filtered off, washed with water and n-butanol and dried under vacuum. Satisfactory elemental analyses were obtained without further purification. In order to obtain crystals large enough for x-ray diffraction studies, the green microcrystalline products were recrystallized from benzene or toluene. Both the nickel and copper complexes are also soluble in chloroform.

Anal. Calcd. for $CuC_9H_{16}N_2O_2$: C, 43.62; H, 6.52; N, 11.31

Found: C, 43.60; H, 6.55; N, 11.37

Calcd. for $NiC_9H_{16}N_2O_2$: C, 44.48; H, 6.65; N, 11.53

Found: C, 44.42; H, 6.73; N, 11.35

Trimeric Nickel(II) Complex of N,N'-Bis(2-Hydroxyethyl)-2,4-Pentanediimine, $Ni_3(DIIMINE)_2(ETAH)_4$

To approximately 50 ml. of 2-aminoethanol, $NH_2CH_2CH_2OH$, was added nickel(II) acetate (0.03 mole), acetylacetone (0.02 mole), and potassium hydroxide (0.06 mole). The resultant slurry was heated at 115°C until everything had dissolved and most of the waters of condensation had been driven off. The mixture was heated further for about thirty minutes until the temperature had risen to 150°C. Heating was

discontinued; the mixture was stoppered and set aside for crystallization. The brown needle crystals which formed after several days were filtered off[2], washed with n-butanol, dried in a vacuum, and stored in a well stoppered bottle. The crystals are subject to slow hydrolysis in air, but good analyses were obtained from the material prepared in this way.

Anal. Calcd. for $Ni_3C_{26}H_{58}N_8O_8$: C,39.68; H, 7.43; N, 14.24

Found: C, 39.16; H, 7.28; N, 13.97

Nickel(II) Complex of N,N'-Bis(2-Hydroxyethyl)-2,4-Pentanediimine and Hydroxide, Ni_2(DIIMINE)(OH)

Into a flask containing 250 ml. of benzene was added (0.005 mole) of $[Ni(H\cdot DIIMINE)]_2$. The mixture was heated near the boiling point of benzene for several hours. The hot solution was filtered in order to remove any unreacted starting material. The red colored filtrate was allowed to stand for several days, after which a red-brown powder, soluble in both methanol and water, separated from the benzene solution. Numerous attempts to obtain single crystals of the product were unsuccessful.

Anal. Calcd. for $Ni_2C_9H_{16}N_2O_3$: C, 34.03; H, 5.07; N, 8.81

Found: C, 33.94; H, 5.09; N, 8.74

Magnetic Studies

Faraday Method

Since all magnetic measurements were made by the Faraday method, a summary of both the mathematical foundation and practical application of the method is in order. In general, if the field gradient across a

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[2] The crystals redissolve if left in contact with the mother liquor for an extended period of time.

sample having an element of volume, ∂v, an element of length, ∂l, and placed in a field of strength, H, is defined as $\partial H/\partial l$, then the force, ∂F, exerted is

$$\partial F = (\kappa_s - \kappa_m) \cdot \partial v \cdot H \frac{\partial H}{\partial l} \tag{1}$$

where κ_s and κ_m are the susceptibilities per unit volume of the sample and the medium respectively. The Faraday method employs special magnet pole pieces (Heyding pole tips) designed to maintain a constant ($H\partial H/\partial l$) over a sizable region inside the magnetic field. In addition, the sample is suspended in an evacuated chamber so that the volume susceptibility of the medium, κ_m, becomes negligibly small, and the expression for the force becomes

$$F = \kappa_s \cdot v \cdot (H \frac{\partial H}{\partial l}) \ . \tag{2}$$

The force exerted on the sample by the magnetic field is measured by observing its change in weight, Δw (in gms.). Consequently, the force, F (in dynes), can be expressed as $g \cdot \Delta w$, where g is the acceleration due to gravity (cm/sec^2).

$$F = g \cdot \Delta w \tag{3}$$

Furthermore, the volume susceptibility, κ , is related to the gram susceptibility, χ_g, by the relationship expressed in equation (4), where ρ is the density and W the weight of the material. Upon substitution of

$$\chi_g = \frac{\kappa}{\rho} = \frac{\kappa v}{W} \tag{4}$$

equations (3) and (4) into (2), one obtains the following expressions for the gram susceptibility.

$$\chi_g = \frac{\Delta w}{W} \cdot \left[\frac{g}{H(\frac{\partial H}{\partial l})}\right]_{CONSTANT} \tag{5}$$

$$\chi_g = \frac{\Delta w}{W} \cdot C \tag{6}$$

The value for C is evaluated by using a weighed amount, W, of a standard of known susceptibility, and observing the difference, Δw, between the weight of the sample in and out of a magnetic field. The standard most generally employed is $HgCo(CNS)_4$ with $\chi_g = 4981.32 \times 10^{-6} \cdot (T + 10)^{-1}$ where T is the absolute temperature (49).

In a typical measurement of the susceptibility, the procedure is to record the weight gain of the standard, Δw_{STD}, at a particular field strength, H. In like manner, the weight gain of the sample, Δw_{SAMPLE}, is determined at the same field strength, H. The gram susceptibility of the sample is then calculated from equation (7).

$$\chi_g^{SAMPLE} = \chi_g^{STD} \cdot \frac{W_{STD}}{W_{SAMPLE}} \cdot \frac{\Delta w_{SAMPLE}}{\Delta w_{STD}} \tag{7}$$

It should be pointed out, however, that the change in weight of both the standard and sample should be corrected for the inherent magnetism of the sample container. Since glass buckets were used in all the

measurements, a positive correction term had to be made to the observed weight changes. In order to determine the magnitude of this correction, a separate measurement of the weight change of the bucket had to be made for each of the different temperatures and field strengths of interest. Once this was done, the gram susceptibility of the sample could be calculated from (7). The value obtained was used to compute the molar susceptibility, χ_m, of the sample by expression (8), where MW is the molecular weight of the complex and the diamagnetic corrections are given by Figgis and Lewis (50). It was then just a simple matter to obtain the

$$\chi_m = \chi_g \cdot MW + \text{DIAMAGNETIC CORRECTIONS} \qquad (8)$$

effective magnetic moment, μ_{eff}, by equation (9), where T is the absolute temperature.

$$\mu_{eff} = 2.84\ (\chi_m \cdot T)^{\frac{1}{2}} \qquad (9)$$

Experimental Apparatus

(1) Cahn #2000 R.G. Automatic Electrobalance and Accessories
(2) Alpha Scientific Model 40-50A Current Regulated Power Supply
(3) Alpha Model 9500 Electromagnet Fitted With Heyding Pole Pieces
(4) Minneapolis-Honeywell Galvanometer (sensitivity equal to 0.0006 μa/mm)

Procedure

The electrobalance was first calibrated to detect weight changes of the magnitude expected for the sample. In general either the 0-10 mg. or 0-20 mg. range was chosen for all of the samples measured in this work.

With the empty glass bucket suspended in the hangdown tube by a nylon thread, and the electromagnet turned off, the electrobalance controls were positioned to the midpoint of their rotations, the mass dial (MD) was set to read 0.0000 and the recorder range set on "Z".[3] The weight of the empty bucket was coarsely counterbalanced with tare weights on the counterbalance pan. A calibration weight equal to one-half the mass dial range (5 or 10 mg.) was included among these tare weights. After the system had been evacuated with a vacuum pump, the galvanometer was nulled at the least sensitive recorder range setting (20 mg.) using the set 0/10 control. The recorder range control was moved to the next most sensitive range (10 mg.) and the galvanometer was again nulled with the set 0/10 dial. This process of raising the recorder sensitivity dial and nulling the galvanometer was continued until the galvanometer could be nulled with the set 0/10 control at the most sensitive recorder range control setting (0.1 mg. for a 10 mg. MDR and 0.2 mg. for a 20 mg. MDR).

Once this was done, the recorder sensitivity control was returned to the "Z" position, the system was opened to the atmosphere, and the calibration weight (5 or 10 mg.) was removed from the counterbalance pan. The mass dial (MD) was set to 0.5000 and the system was re-evacuated. The galvanometer was nulled at subsequently more sensitive recorder range settings using the set 5 control. When it was possible to null the galvanometer at the most sensitive recorder range setting using the set 5 control, the sensitivity control was returned to the "Z" position, the system was again opened to the air, the mass dial (MD) set to 0.0000, and

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[3]The recorder range control had to be returned to the "Z" position whenever weights were added to or removed from the counterbalance pan.

the calibration weight (5 or 10 mg.) set back onto the counterbalance pan. Upon re-evacuation, the galvanometer was nulled once again at the most sensitive recorder range with the set 0/10 control. This procedure was continued until the galvanometer nulled at both the mass dial settings (0.0000 and 0.5000) without further need of resetting the set 5 or set 0/10 controls. The galvanometer was considered nulled when the hairline did not deviate by more than $\pm$ 2 divisions (1 division = 1 mm) from the null point at either mass dial (MD) setting. When this condition was achieved, the set 5 and set 0/10 controls were locked down and the calibration was considered complete.

After calibrating the electrobalance, the magnet was energized and diamagnetic corrections for the glass bucket were determined at the various current settings, J, of the electromagnet and each temperature of interest. This was done by removing the (5 or 10 mg.) calibration weight from the counterbalance pan, evacuating the system, setting the mass dial (MD) at 0.5000 and recording the mass dial (MD) settings required to null the galvanometer at each current setting of the magnet (J = 0, 4, 5, 6, 7, 8, 9, and 10).[4] Diamagnetic corrections for the bucket were obtained in this manner at each of three different temperatures (298, 193 and 77°K).

The next step was to equate changes in the mass dial (MD) readings on the electrobalance with some value of the susceptibility at each current setting. This was done by recording the mass dial (MD) reading required to null the detector at each J setting with the bucket loaded

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[4]The position of the magnet relative to the bucket had to be determined beforehand so as to place the bucket in a region of constant force.

with a standard of known magnetic susceptibility. The standard chosen was mercury tetrathiocyanatocobaltate, $Hg(SCN)_4Co$, which has a susceptibility of 16.44×10^{-6} at 293°K (49).

The bucket was loaded with a known weight of standard (~40 mg.) and suspended from the nylon thread down the hangdown tube. The (5 or 10 mg.) calibration weight was returned to the counterbalance pan along with enough tare weights to counterbalance the weight of standard loaded into the bucket. The system was evacuated and the galvanometer restored to the null position with the mass dial (MD) at each of the J current settings; namely, 0, 4, 5, 6, 7, 8, 9, and 10. Readings of this type were recorded at each of three temperatures (298, 197 and 77°K). Afterwards, the bucket was cleansed with nitric acid, washed with water and methanol, and dried in air.

The samples were run in the same manner as was the standard. The amount of sample used was approximately the same as that weighed out for the standard. Mass dial (MD) readings were recorded for current settings of 0, 4, 5, 6, 7, 8, 9, and 10 at each temperature of interest. Since there was no way of measuring the temperature of the sample directly, sufficient cooling time was allowed (approximately four hours) before measurements were recorded. During the waiting period, an adequate amount of coolant of known temperature was maintained in the chamber surrounding the hangdown tube. After the waiting period, mass dial (MD) readings were taken at each current setting. After another hour, a second set of readings was taken and compared with the first set of readings. An hour later a third set of readings was taken and compared to the second. This procedure was continued until no significant differences in

the mass dial readings could be observed between one set of measurements and another.

Calculations

The equations used for calculating the magnetic moment of a complex at a given absolute temperature, T, are given below. The meaning of each of the symbols used in these equations is also defined.

$$DMB(J) = [MDB(J) - MDB(0)] \cdot MDR \cdot 10^{-3};\ g$$

$$DMSTD(J) = [MDSTD(J) - MDSTD(0)] \cdot MDR \cdot 10^{-3} - DMB(J);\ g$$

$$DMSAM(J) = [MDSAM(J) - MDSAM(0)] \cdot MDR \cdot 10^{-3} - DMB(J);\ g$$

$$KAPPA(J) = [DMSTD(J)/(GMSTD \cdot XGSTD(T))];\ g$$

$$XGSAM(J) = [DMSAM(J)/(KAPPA(J) \cdot GMSAM)];\ g^{-1}$$

$$XMSAM(J) = [(XGSAM(J) \cdot EQUIV) + DIAMAG];\ m^{-1}$$

$$\mu_{eff}^{T}(J) = 2.84(XMSAM(J) \cdot T)^{\frac{1}{2}};\ B.M.$$

MDR = mass dial range; mg

MDB(J) = mass dial reading for the bucket at current setting, J; unitless

DMB(J) = change in weight of the bucket produced on application of the magnetic field at current setting, J; g

MDSTD(J) = mass dial reading for the standard at current setting J; unitless

DMSTD(J) = change in weight of the standard produced on application of the magnetic field at current setting, J; g

MDSAM(J) = mass dial reading for the sample at current setting, J; unitless

GMSTD = amount of $Hg(SCN)_4Co$ standard weighed out; g

DMSAM(J) = change in weight of the sample produced on application of the magnetic field at current setting, J; g

XGSTD(T) = gram susceptibility of $Hg(SCN)_4Co$ standard at absolute temperature, T; $g^{-1}deg^{-1}$; calculated from the expression: $XGSTD(T) = (4981.32 \times 10^{-6})/(T + 10)$

KAPPA(J) = ratio of the change in weight of the standard at current setting, J, to the total susceptibility of the standard; g

GMSAM = amount of sample weighed out; g

XGSAM(J) = gram susceptibility of the sample observed at current setting, J; g^{-1}

EQUIV = sum of the gram atomic weights for the molecular species under consideration (generally the weight per metal ion); $g\text{-}m^{-1}$

XMSAM(J) = susceptibility of the sample observed at current setting, J; m^{-1}

DIAMAG = diamagnetic corrections for the ligand obtained from the atomic values given by Figgis and Lewis (50); m^{-1}

$\mu_{eff}^{T}(J)$ = effective magnetic moment of the sample observed at current setting, J, and temperature, T; B.M.

Magnetic Data

The magnetic data obtained from measurements on the complexes reported in Part I of this work are shown in Tables 2 thru 6.

Crystallographic Studies

Calculations

Computations were performed on a Burroughs 5500 computer and on a Univac 1108 computer. The programs used were modified versions of

Table 2. Magnetic Data for $[Cu(H\cdot DIIMINE)]_2$ at 298°K

Current	Susceptibility per Gram of Complex	Susceptibility per Gram-Atom Copper	Magnetic Moment per Gram-Atom Copper
J	$\chi_g \times 10^6$	$\chi_m \times 10^6$	$\mu_{eff}^{298°K}$; B.M.
3	4.452	1207.	1.701
4	4.426	1201.	1.696
5	4.420	1199.	1.695
6	4.437	1204.	1.698
7	4.439	1204.	1.698
8	4.398	1194.	1.691
9	4.420	1199.	1.695
10	4.417	1199.	1.695

Average $\mu_{eff}^{298°K} = 1.69(1)$ B. M.

EQUIV = 247.73 g-m^{-1}; formula weight divided by two

DIAMAG = 104.84 x 10^{-6} m^{-1}; calculated for one-half a formula unit

FORMULA UNIT = $[Cu(H\cdot DIIMINE)]_2$

Table 3. Magnetic Data for $[Cu(H\cdot DIIMINE)]_2$ at 193°K

Current	Susceptibility per Gram of Complex	Susceptibility per Gram-Atom Copper	Magnetic Moment per Gram-Atom Copper
J	$\chi_g \times 10^6$	$\chi_m \times 10^6$	$\mu_{eff}^{193°K}$; B.M.
3	5.776	1535.	1.546
4	5.915	1570.	1.563
5	5.930	1573.	1.565
6	5.865	1557.	1.557
7	5.911	1569.	1.563
8	5.903	1567.	1.562
9	5.898	1565.	1.561
10	5.870	1559.	1.558

Average $\mu_{eff}^{193°K} = 1.56(2)$ B. M.

Table 4. Magnetic Data for $[Cu(H\cdot DIIMINE)]_2$ at 77°K

Current	Susceptibility per Gram of Complex	Susceptibility per Gram-Atom Copper	Magnetic Moment per Gram-Atom Copper
J	$\chi_g \times 10^6$	$\chi_m \times 10^6$	$\mu_{eff}^{77°K}$; B.M.
3	7.511	1965.	1.105
4	7.891	2059.	1.131
5	8.039	2096.	1.141
6	8.171	2128.	1.150
7	8.091	2109.	1.145
8	8.112	2114.	1.146
9	8.096	2110.	1.145

Average $\mu_{eff}^{77°K} = 1.14(4)$ B.M.

Table 5. Magnetic Data for Ni_2(DIIMINE)(OH) at 298°K

Current	Susceptibility per Gram of Complex	Susceptibility per Formula Unit	Magnetic Moment per Formula Unit
J	$\chi_g \times 10^6$	$\chi_m \times 10^6$	$\mu_{eff}^{298°K}$; B.M.
4	12.242	4023.4	3.109
5	12.159	3997.0	3.099
6	12.095	3976.4	3.091
7	12.150	3994.2	3.098
8	12.106	3980.2	3.093
9	12.102	3978.9	3.093
10	12.070	3968.8	3.090

Average $\mu_{eff}^{298°K} = 3.09(2)$ B.M.

EQUIV = 317.622 g-m^{-1}; formula weight

DIAMAG = 135.05 x 10^{-6} m^{-1}; calculated for one formula units

FORMULA UNIT = Ni_2(DIIMINE)(OH)

Table 6. Magnetic Data for Ni_2(DIIMINE)(OH) at 77°K

Current	Susceptibility per Gram of Complex	Susceptibility per Formula Unit	Magnetic Moment per Formula Unit
J	$\chi_g \times 10^6$	$\chi_m \times 10^6$	$\mu_{eff}^{77°K}$; B.M.
4	42.240	13551.	2.901
5	42.222	13545.	2.900
6	42.265	13559.	2.902
7	42.304	13571.	2.903
8	42.597	13665.	2.913
9	41.981	13469.	2.892
10	42.103	13508.	2.896

Average $\mu_{eff}^{77°K}$ = 2.901(5) B.M.

Zalkin's FORDAP Fourier summation program (51) and Busing, Martin and Levy's ORFFE (52) and XFLS(53). The other programs used, include Stewart's ABSORB routine in XRAY-70 (54); Bertrand's program (55) for calculating Lorentz-polarization corrections; Bertrand and Kelly's program (56) for calculating the least-squares plane for a set of atoms; Johnson's ORTEP (57) for drawing crystal structure illustrations; and a modified version of Carter's program (58) for calculating unit cell parameters and generating control cards for the Picker four-angle programmer.

Solution of the Structure of $Co(DIIMINE)(ETAH)_2$[5]

A dark-red needle crystal of approximate dimensions 0.2 x 0.2 x 0.7 mm. was placed inside a Lindeman Capillary tube, sealed with a small flame, and mounted on a glass fiber with the long dimension of the crystal parallel to the fiber. Precession photographs indicated a triclinic crystal, P1 or $P\bar{1}$. Space group $P\bar{1}$ was assumed and the successful refinement of the structure later confirmed this choice.

The crystal was transferred to a Picker four-circle diffractometer from which the unit cell parameters were obtained by a least-squares refinement of 22 reflections. The cell parameters obtained were: $a = 12.677(1)$Å, $b = 9.187(1)$Å, $c = 9.364(1)$Å, $\alpha = 121.70(8)^\circ$, $\beta = 81.26(8)^\circ$, $\gamma = 115.64(8)^\circ$, and $V = 832.68$Å^3 (25°C, molybdenum radiation, $\lambda = 0.7107$Å). A Delaunay reduction based on these parameters

[5]The general method of data collection and reduction employed in this structure determination has been used in all the structure determinations reported in this work. Many of the equations, definitions and experimental techniques to be mentioned here will be equally valid in subsequent references made to them. Any exceptions to this will be noted.

revealed no additional symmetry. The reduced cell obtained had the following dimensions: $a' = 12.677$Å, $b' = 9.039$Å, $c' = 9.364$Å, $\alpha' = 120.13^\circ$, $\beta' = 98.74^\circ$ and $\gamma' = 106.41^\circ$. The transformation matrix is:

$$\begin{bmatrix} a' \\ b' \\ c' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

The calculated density of 1.46 g-cm^{-3} based on two formula units per unit cell, agreed well with the observed density of 1.45(1) g-cm^{-3} measured by the flotation method using a mixture of n-heptane and carbon tetrachloride.

Intensity measurements were made on the diffractometer with a scintillation counter mounted 21 cm. from the crystal by the $\theta - 2\theta$ scan technique, using a takeoff angle of 1.6° and a scan rate of 1° per minute. A symmetric scan of 2° was taken about the calculated position and stationary background counts of 20 seconds were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of data; the attenuators were calibrated by collecting intensities on 30 different reflections of various magnitudes. The threshold point was set so that the counting rate would not exceed 10,000 counts per second and the pulse height analyzer was set for approximately a 90% window centered on the Mo Kα peak. A total of 5114 reflections were collected. Corrected intensities (I) were obtained by subtracting three times the actual measured background from the total

peak count (CT). The factor of three in the calculation arises from the

$$I = CT - 3(bgd1 + bgd2) \tag{10}$$

peak scan time being three times as long as the total background count time. The corrected intensities were assigned standard deviations according to the formula (59) represented in equation (11), where t_c is

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(bgd1 + bgd2) + (pI)^2]^{\frac{1}{2}} \tag{11}$$

the scan time and t_b is the counting time of each background (either bgd1 or bgd2). The ignorance factor, p, was assigned a value of 0.01. A total of 3210 reflections was accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.30. The intensities were corrected for Lorentz and polarization effects. A linear absorption coefficient, μ, of 10.9 cm^{-1} was calculated for the crystal according to the expression given in equation (12), where ρ is the density ($g\text{-}cm^{-3}$), g_i is

$$\mu = \Sigma_i \, g_i(\mu/\rho)_{i,Mo} \tag{12}$$

the mass fraction of element, i, and $(\mu/\rho)_{i,Mo}$ is the mass absorption coefficient for element, i, and molybdenum radiation, Mo. The values used for the mass absorption coefficients were those tabulated in the International Tables for X-Ray Crystallography (60). The value of μ so calculated was not considered large enough to significantly affect the data,

therefore, the intensities were not corrected for absorption. The intensities of two standard reflections (5,0,0 and -6,7,-6) were measured at intervals of 100 reflections and showed no significant variation during the data collection.

A three-dimensional Patterson function was calculated using the over 3000 unique nonzero reflections. A set of positions for the cobalt atoms was chosen from the Patterson function and a subsequent electron density calculation phased on this set of atoms revealed the positions of all the remaining non-hydrogen atoms. With two formula units per unit cell, the asymmetric unit consisted of one formula unit. Consequently, atomic positions had to be located for only one formula unit. In the structure factor calculations, the scattering factor tables of Ibers were employed (60) for all the atoms.

Full-matrix least-squares refinement of a scale factor, coordinates and anisotropic temperature factors for all atoms was carried out using a weighting scheme based on counting statistics ($w_i = 4I/\sigma(I)^2$) and minimizing $\Sigma_i\ w_i(|F_o| - |F_c|)^2$; the refinement converged to a weighted residual, R_2, $(\{\Sigma_i\ w_i(|F_o| - |F_c|)^2 / \Sigma_i\ w_i(|F_o|)^2\}^{\frac{1}{2}})$, of 0.0593 and a conventional residual, R_1, $(\Sigma||F_o| - |F_c|| / \Sigma\ |F_o|)$, of 0.0596. The positional parameters from the last cycles of least-squares refinement are presented in Table 7, and the final thermal parameters are presented in Table 8. The observed and calculated structure factors for all 3197 unique nonzero reflections are given in Table 9.

Solution of the Structure of $[Ni(H\cdot DIIMINE)]_2$

A green crystal of approximate dimensions 0.65 x 0.10 x 0.10 mm. was glued to a glass fiber with clear nail polish. The crystal was posi-

Table 7. Final Positional Parameters for Co(DIIMINE)$(ETAH)_2$

Atom	x	y	z
Co	0.15793(5)	-0.07136(8)	-0.23311(7)
AC1	0.4810(5)	-0.127(1)	-0.272(1)
AC2	0.3944(3)	-0.0447(7)	-0.2503(5)
AC3	0.4381(4)	0.1264(7)	-0.2452(6)
AC4	0.3728(4)	0.2187(6)	-0.2375(5)
AC5	0.4394(5)	0.4048(9)	-0.2319(8)
E1N	0.2821(3)	-0.1376(5)	-0.2409(4)
E1C1	0.2386(5)	-0.3220(7)	-0.2535(8)
E1C2	0.1215(4)	-0.3520(7)	-0.1784(7)
E1O	0.0550(2)	-0.3018(4)	-0.2370(4)
E2N	0.2568(3)	0.1520(5)	-0.2353(4)
E2C1	0.1930(5)	0.2568(8)	-0.2237(7)
E2C2	0.0670(5)	0.135(1)	-0.257(1)
E2O	0.0297(2)	-0.0118(4)	-0.2294(4)
E3N	0.1699(3)	0.0773(5)	0.0158(4)
E3C1	0.2767(4)	0.1418(7)	0.1199(5)
E3C2	0.2770(4)	0.2726(8)	0.3052(5)
E3O	0.1879(3)	0.1892(7)	0.3822(5)
E4N	0.1260(3)	-0.2272(5)	-0.4830(4)
E4C2	0.1842(4)	-0.3544(6)	-0.7749(5)
E4C1	0.2177(4)	-0.1929(6)	-0.5949(5)
E4O	0.1646(3)	-0.5271(5)	-0.7911(4)

Table 8. Final Anisotropic Thermal Parameters ($\times 10^4$) for $Co(DIIMINE)(ETAH)_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	35.3(4)	88(1)	65.3(8)	27.9(5)	13.4(3)	45.7(7)
AC1	67(4)	383(20)	299(16)	115(8)	37(6)	181(15)
AC2	43(3)	189(10)	110(7)	44(4)	11(3)	67(7)
AC3	43(3)	204(11)	154(8)	14(4)	12(4)	98(8)
AC4	66(3)	113(8)	82(6)	9(4)	10(3)	40(6)
AC5	98(5)	177(12)	240(13)	2(6)	31(6)	141(11)
E1N	45(2)	120(7)	107(5)	38(3)	15(3)	60(5)
E1C1	78(4)	150(10)	263(12)	64(5)	21(5)	123(9)
E1C2	65(3)	175(10)	239(11)	29(5)	2(5)	158(10)
E1O	49(2)	135(6)	140(5)	22(3)	5(2)	98(5)
E2N	59(3)	108(7)	77(5)	35(3)	20(3)	55(5)
E2C1	108(5)	180(10)	165(9)	90(6)	52(5)	122(9)
E2C2	72(5)	259(16)	546(25)	48(7)	-15(8)	280(3)
E2O	53(2)	205(7)	118(5)	68(3)	31(2)	109(5)
E3N	43(2)	148(7)	77(5)	42(3)	9(2)	61(5)
E3C1	53(3)	214(10)	97(6)	56(4)	-1(3)	60(7)
E3C2	64(3)	219(11)	92(6)	55(5)	4(3)	69(7)
E3O	77(3)	430(14)	143(6)	47(5)	5(3)	181(8)
E4N	50(2)	123(7)	69(5)	28(3)	18(2)	42(5)
E4C2	60(3)	157(9)	87(6)	40(4)	17(3)	57(6)
E4C1	66(3)	137(8)	81(6)	24(4)	27(3)	49(6)
E4O	69(2)	145(6)	176(6)	59(3)	33(3)	74(5)

Table 9. Observed and Calculated Structure Factors for Co(DIIMINE)$(ETAH)_2$

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
	L=-13			0	9	5	6	-6	6	7	6	-5	1	9	9
				-7	10	5	5	-5	6	10	9	-2	1	10	12
-4	6	7	7	-4	10	11	10	-4	6	22	21	-1	1	10	12
-3	6	5	4	-3	10	9	9	-3	6	12	11	0	1	6	7
-4	7	7	8					-2	6	5	6	1	1	10	10
-1	7	6	5		L=-11			-1	6	13	13	2	1	9	10
-3	8	8	8					0	6	8	6	4	1	6	8
-2	8	5	7	-1	0	12	12	2	6	10	11	7	1	10	10
				0	0	14	14	3	6	6	8	8	1	16	17
	L=-12			2	0	7	7	5	6	6	7	-8	2	7	7
				3	0	6	5	6	6	8	8	-7	2	9	8
-2	2	5	5	-1	1	7	7	-9	7	6	5	-5	2	8	9
-1	2	12	11	0	1	5	6	-7	7	10	12	-4	2	9	9
0	2	5	3	6	1	7	7	-6	7	18	20	-2	2	9	8
2	2	9	7	-6	2	6	8	-4	7	18	20	-1	2	12	11
2	3	6	6	1	2	9	9	-3	7	11	12	1	2	5	4
3	3	6	8	3	2	6	7	-1	7	9	9	2	2	13	14
-6	4	6	7	4	2	7	8	2	7	10	11	3	2	9	9
0	4	11	11	6	2	8	8	3	7	13	15	5	2	11	13
2	4	6	5	7	2	10	10	5	7	9	9	6	2	14	15
3	4	12	12	-8	3	8	8	-10	8	6	6	8	2	16	16
-6	5	6	7	-6	3	8	8	-9	8	6	5	9	2	11	11
-3	5	7	8	-5	3	10	10	-7	8	7	8	-8	3	7	8
-2	5	10	10	0	3	8	7	-6	8	12	12	-7	3	12	13
0	5	10	13	1	3	16	18	-3	8	5	5	-6	3	9	8
1	5	9	11	2	3	8	8	0	8	6	6	-5	3	6	8
3	5	11	12	3	3	5	7	1	8	6	5	-4	3	10	11
4	5	7	7	4	3	13	14	2	8	6	6	-1	3	11	12
-8	6	6	6	5	3	7	7	3	8	11	12	0	3	12	13
-6	6	11	11	7	3	8	11	4	8	6	5	2	3	17	18
-5	6	14	14	-9	4	5	5	-10	9	6	7	3	3	16	16
-3	6	10	10	-8	4	9	9	-9	9	8	9	5	3	8	10
-2	6	12	12	-7	4	7	7	-3	9	8	9	6	3	10	10
-1	6	5	4	-6	4	6	7	-2	9	9	11	9	3	11	13
1	6	13	13	-5	4	11	11	0	9	7	9	-10	4	12	11
2	6	8	8	-2	4	8	10	1	9	8	10	-9	4	6	7
3	6	6	7	-1	4	8	9	-11	10	10	10	-7	4	15	14
4	6	13	13	0	4	10	8	-9	10	5	5	-6	4	16	16
-9	7	7	7	1	4	18	17	-6	10	6	4	-4	4	9	10
-8	7	6	8	2	4	14	14	-5	10	11	11	-3	4	13	14
-6	7	10	12	4	4	12	12	-4	10	5	4	-1	4	19	19
-5	7	14	17	5	4	7	6	-3	10	9	10	0	4	24	25
-2	7	7	7	6	4	5	3	-2	10	13	13	2	4	15	14
1	7	7	6	-8	5	8	10	-6	11	5	5	3	4	18	18
2	7	8	8	-7	5	6	7	-5	11	12	13	5	4	6	4
-8	8	10	8	-5	5	11	11	-2	11	9	9	7	4	7	6
-7	8	8	8	-4	5	8	9					9	4	8	9
-6	8	6	4	-2	5	8	10		L=-10			-12	5	10	9
-5	8	12	13	-1	5	14	15					-10	5	8	11
-4	8	7	9	2	5	14	16	-5	0	5	5	-9	5	6	7
-2	8	10	11	3	5	6	7	-1	0	6	6	-7	5	8	8
1	8	8	7	6	5	11	12	2	0	7	6	-6	5	15	16
2	8	10	11	-11	6	8	7	4	0	8	8	-5	5	9	8
-4	9	11	12	-10	6	7	7	7	0	9	9	-4	5	9	10
-3	9	6	6	-8	6	7	7	8	0	8	9	-3	5	18	20
-1	9	8	10	-7	6	10	10	-7	1	5	6	-2	5	8	9

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-1	5	12	14	-5	10	10	9	7	2	14	14	-1	6	14	15
0	5	17	19	-4	10	19	19	9	2	8	7	0	6	6	4
1	5	8	9	-3	10	11	11	10	2	6	5	1	6	9	9
3	5	16	17	-2	10	6	5	-12	3	6	6	2	6	14	15
-12	6	11	10	-1	10	11	11	-11	3	5	5	3	6	9	9
-9	6	6	5	0	10	7	7	-9	3	16	15	4	6	5	5
-8	6	5	4	-12	11	6	6	-8	3	9	8	5	6	15	14
-6	6	17	17	-10	11	8	9	-6	3	20	20	6	6	12	12
-5	6	14	14	-7	11	9	9	-5	3	22	22	7	6	6	5
-4	6	5	3	-6	11	10	10	-3	3	11	12	8	6	11	11
-3	6	12	10	-4	11	13	14	-2	3	14	15	-13	7	10	11
-2	6	9	8	-3	11	8	10	0	3	18	18	-12	7	7	6
-1	6	8	6	-9	12	8	8	1	3	24	23	-10	7	8	8
1	6	12	12	-6	12	10	10	2	3	7	6	-9	7	6	6
2	6	5	6					3	3	12	12	-8	7	5	3
3	6	10	10		L=-9			4	3	16	17	-7	7	15	15
4	6	11	11					5	3	5	3	-6	7	22	22
6	6	8	7	-7	0	5	6	6	3	11	11	-5	7	10	11
7	6	9	8	-4	0	6	6	9	3	6	6	-4	7	27	27
-13	7	5	3	-3	0	6	4	-12	4	9	9	-3	7	13	13
-12	7	6	5	-1	0	19	19	-11	4	7	6	-1	7	12	11
-9	7	7	7	0	0	17	18	-9	4	12	12	0	7	5	2
-6	7	12	13	1	0	7	6	-8	4	10	10	2	7	13	14
-5	7	13	14	2	0	11	11	-7	4	7	7	3	7	20	20
2	7	7	6	3	0	9	11	-6	4	12	13	5	7	11	12
4	7	10	12	5	0	8	8	-5	4	13	13	6	7	12	13
5	7	8	8	6	0	14	13	0	4	10	9	-13	8	10	10
-13	8	5	4	7	0	10	9	1	4	18	18	-12	8	6	5
-11	8	10	10	8	0	12	12	2	4	15	15	-10	8	11	11
-10	8	7	6	9	0	19	19	4	4	15	16	-9	8	6	5
-7	8	8	8	10	0	7	7	7	4	5	6	-7	8	11	11
-5	8	10	11	-6	1	6	7	8	4	7	8	-6	8	15	15
-4	8	8	8	-4	1	7	7	10	4	8	8	-5	8	6	6
-2	8	13	12	-3	1	11	10	-11	5	7	7	-4	8	10	10
-1	8	5	5	-2	1	9	8	-10	5	5	4	-3	8	12	12
1	8	14	13	-1	1	19	19	-8	5	9	9	-1	8	9	9
2	8	15	15	0	1	19	19	-7	5	5	5	0	8	11	10
4	8	11	12	1	1	7	6	-6	5	8	7	1	8	6	5
5	8	12	11	3	1	13	14	-5	5	6	7	3	8	17	17
-11	9	11	12	6	1	15	14	-1	5	14	14	4	8	10	9
-10	9	8	8	7	1	19	17	1	5	7	8	-13	9	9	9
-8	9	6	5	9	1	14	14	2	5	20	21	-12	9	12	12
-7	9	8	7	10	1	11	10	4	5	5	5	-10	9	14	13
-5	9	7	8	-9	2	11	10	6	5	11	10	-9	9	16	14
-4	9	13	14	-7	2	11	11	7	5	6	6	-7	9	6	6
-3	9	6	4	-6	2	19	19	8	5	14	14	-6	9	12	13
-2	9	10	11	-5	2	7	8	9	5	9	8	-5	9	7	7
-1	9	13	15	-4	2	10	9	-14	6	5	6	-3	9	22	23
2	9	13	15	-3	2	21	20	-13	6	8	8	-2	9	14	15
3	9	7	8	-2	2	15	14	-10	6	10	10	-1	9	6	6
-13	10	9	9	-1	2	9	9	-8	6	10	9	0	9	18	18
-11	10	9	10	0	2	24	23	-7	6	10	10	1	9	14	14
-10	10	14	15	1	2	20	18	-5	6	16	15	3	9	13	13
-8	10	7	6	3	2	19	20	-4	6	25	24	4	9	8	7
-7	10	11	10	4	2	11	12	-3	6	10	9	-13	10	8	7
-6	10	6	6	6	2	15	14	-2	6	10	9	-12	10	13	14

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-11	10	9	10	-9	2	7	6	1	5	5	5	-1	8	6	7
-10	10	6	4	-8	2	11	10	2	5	8	7	0	8	10	5
-9	10	12	13	-7	2	8	7	3	5	24	23	1	8	19	19
-8	10	9	9	-6	2	5	4	4	5	7	6	2	8	14	14
-6	10	14	13	-5	2	16	16	6	5	13	13	4	8	16	16
-5	10	15	15	-4	2	11	11	7	5	15	14	-14	9	7	7
-3	10	18	17	-2	2	8	6	9	5	12	13	-12	9	11	10
-2	10	16	16	-1	2	7	7	10	5	14	15	-11	9	18	18
0	10	7	7	0	2	8	8	-15	6	5	7	-10	9	10	8
1	10	6	6	2	2	18	18	-13	6	10	10	-9	9	7	7
-12	11	7	8	3	2	17	16	-12	6	9	10	-8	9	10	10
-11	11	10	10	5	2	18	18	-7	6	5	4	-5	9	6	7
-9	11	7	7	6	2	11	10	-6	6	24	24	-4	9	8	8
-8	11	7	7	7	2	11	9	-5	6	20	21	-2	9	12	13
-6	11	7	7	8	2	17	16	-4	6	7	7	-1	9	15	15
-5	11	12	12	9	2	6	5	-3	6	25	25	1	9	9	9
-4	11	6	4	11	2	7	6	-2	6	17	17	2	9	14	15
-2	11	7	8	-10	3	6	7	-1	6	5	6	4	9	5	6
-11	12	8	6	-8	3	14	13	0	6	12	12	-14	10	7	7
				-7	3	23	22	1	6	21	20	-13	10	7	7
	L=-8			-6	3	9	9	2	6	7	8	-11	10	16	15
				-5	3	17	17	3	6	19	18	-10	10	16	16
-9	0	13	12	-4	3	11	11	4	6	22	22	-8	10	8	8
-8	0	8	8	-2	3	4	4	5	6	9	8	-7	10	5	6
-6	0	7	6	-1	3	9	7	6	6	10	9	-5	10	8	8
-5	0	11	11	0	3	16	16	7	6	14	15	-4	10	15	16
-3	0	10	11	2	3	27	26	8	6	6	6	-3	10	9	9
-2	0	18	18	3	3	17	17	-15	7	11	11	-2	10	6	6
-1	0	11	11	5	3	13	14	-14	7	5	6	-1	10	9	9
0	0	28	27	6	3	5	5	-13	7	7	6	0	10	5	5
1	0	24	24	8	3	11	12	-12	7	12	13	-13	11	8	8
2	0	7	6	9	3	13	13	-11	7	7	8	-12	11	7	5
3	0	9	9	11	3	10	10	-9	7	14	14	-11	11	7	5
4	0	16	14	-13	4	6	5	-8	7	11	11	-10	11	6	7
6	0	7	6	-12	4	6	5	-6	7	31	31	-7	11	6	7
7	0	15	15	-10	4	16	16	-5	7	36	36	-6	11	9	8
8	0	13	10	-9	4	12	11	-3	7	17	17	-4	11	12	13
9	0	5	4	-7	4	21	21	-2	7	19	20	-3	11	6	6
10	0	8	9	-6	4	16	15	1	7	14	13	-10	12	6	4
-11	1	9	10	-3	4	6	6	2	7	8	6	-9	12	8	7
-9	1	11	12	-1	4	22	22	3	7	16	16	-6	12	9	10
-5	1	18	17	0	4	21	21	4	7	17	18	-3	12	11	11
-4	1	6	5	1	4	15	15	5	7	6	7				
-3	1	9	8	2	4	19	18	6	7	6	6		L=-7		
-2	1	29	29	3	4	16	15	-15	8	8	8				
-1	1	20	20	7	4	9	8	-14	8	11	10	-11	1	5	4
0	1	20	19	8	4	10	10	-12	8	11	12	-10	1	8	8
1	1	19	20	9	4	15	15	-11	8	16	16	-9	1	8	7
2	1	15	16	10	4	8	8	-10	8	5	5	-7	1	11	11
3	1	6	5	-13	5	9	8	-9	8	13	12	-6	1	14	13
4	1	13	12	-6	5	13	13	-8	8	14	13	-4	1	15	15
5	1	8	9	-4	5	14	14	-7	8	12	12	-1	1	22	22
7	1	20	18	-3	5	19	19	-6	8	14	13	0	1	13	12
8	1	19	17	-2	5	5	2	-5	8	21	21	3	1	8	9
-12	2	7	7	-1	5	24	25	-4	8	11	10	4	1	8	7
-11	2	7	5	0	5	22	22	-2	8	18	19	5	1	8	6

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
6	1	10	10	-4	4	12	11	-10	7	11	12	4	10	10	10
7	1	9	8	-3	4	10	9	-8	7	14	15	-12	11	7	7
8	1	6	6	-2	4	17	16	-7	7	21	21	-11	11	8	8
9	1	18	18	-1	4	14	13	-6	7	18	18	-9	11	8	7
10	1	8	6	0	4	30	28	-5	7	25	25	-8	11	10	10
12	1	7	7	1	4	42	41	-4	7	29	28	-6	11	11	10
-13	2	7	7	2	4	26	24	-3	7	12	12	-5	11	17	17
-11	2	6	4	3	4	7	7	-2	7	6	5	-3	11	5	6
-9	2	16	16	4	4	30	30	-1	7	5	5	-2	11	11	12
-8	2	5	3	7	4	12	13	1	7	4	2	-1	11	6	4
-7	2	22	21	8	4	15	15	2	7	12	13	-11	12	7	8
-6	2	24	24	10	4	13	13	3	7	17	17	-8	12	7	8
-4	2	16	17	11	4	18	18	5	7	11	12	-5	12	7	8
-3	2	14	15	-14	5	10	11	6	7	9	9	-2	12	12	12
-2	2	5	5	-12	5	12	11	-16	8	6	6				
-1	2	13	13	-11	5	13	13	-14	8	10	9		L=-6		
0	2	22	23	-2	5	22	24	-13	8	13	12				
1	2	8	7	-1	5	28	28	-12	8	5	6	-12	1	5	5
2	2	15	14	0	5	9	8	-11	8	6	7	-11	1	8	9
3	2	18	18	1	5	29	29	-10	8	17	18	-9	1	10	10
6	2	17	15	2	5	35	35	-8	8	9	8	-8	1	12	11
7	2	20	19	4	5	18	18	-7	8	11	10	-5	1	8	9
9	2	15	14	5	5	8	7	-6	8	9	8	-4	1	9	8
10	2	11	10	6	5	7	6	-5	8	11	10	-3	1	5	2
11	2	5	3	7	5	11	11	-3	8	9	9	-2	1	31	32
12	2	6	6	8	5	13	13	-1	8	10	6	1	1	23	23
13	2	5	6	9	5	8	7	2	8	9	9	2	1	13	14
-14	3	5	3	10	5	5	4	3	8	12	13	3	1	11	10
-11	3	5	4	11	5	10	10	4	8	5	4	4	1	10	9
-9	3	14	14	-16	6	6	3	7	8	6	4	5	1	13	12
-7	3	4	4	-14	6	15	15	-13	9	8	8	7	1	30	29
-6	3	20	20	-13	6	10	10	-12	9	15	15	8	1	33	31
-5	3	21	20	-12	6	8	8	-10	9	13	14	10	1	13	13
-3	3	7	7	-11	6	15	15	-9	9	11	11	11	1	11	10
-2	3	11	12	-10	6	12	11	-6	9	5	6	12	1	8	7
0	3	26	24	-9	6	6	6	-4	9	8	8	13	1	6	6
1	3	23	22	-8	6	22	22	-3	9	18	20	14	1	9	10
3	3	14	13	-7	6	19	18	-2	9	7	7	-14	2	7	7
4	3	22	20	-6	6	6	7	-1	9	12	11	-13	2	5	5
5	3	13	11	-5	6	41	42	0	9	14	15	-9	2	5	4
6	3	11	10	-4	6	39	40	1	9	8	9	-8	2	4	4
7	3	13	13	-2	6	22	23	3	9	12	13	-5	2	17	16
8	3	9	9	-1	6	22	23	-15	10	6	4	-4	2	21	20
9	3	9	9	0	6	5	6	-13	10	7	7	-2	2	17	16
10	3	12	12	1	6	16	18	-12	10	10	11	-1	2	19	20
11	3	9	9	2	6	25	25	-11	10	7	6	1	2	17	16
-15	4	7	6	3	6	9	10	-10	10	5	5	2	2	40	38
-14	4	8	8	4	6	17	16	-9	10	11	11	3	2	15	15
-13	4	6	4	5	6	19	19	-8	10	7	7	4	2	24	23
-12	4	8	8	6	6	7	7	-6	10	15	15	5	2	38	37
-11	4	7	7	7	6	11	10	-5	10	12	12	6	2	13	12
-9	4	12	12	8	6	9	8	-4	10	7	8	7	2	23	22
-8	4	9	9	-16	7	6	6	-3	10	22	21	8	2	27	26
-7	4	13	13	-14	7	15	15	-2	10	11	11	9	2	11	9
-6	4	16	14	-13	7	12	12	0	10	9	8	11	2	10	9
-5	4	21	21	-11	7	8	7	1	10	6	6	12	2	9	9

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-14	3	12	12	-2	5	5	5	-5	8	19	19		L=-5		
-13	3	9	9	-1	5	20	20	-4	8	7	7				
-10	3	11	12	0	5	25	27	-3	8	5	5	-13	1	12	12
-8	3	26	25	1	5	12	13	-2	8	14	15	-11	1	10	9
-7	3	35	34	2	5	8	10	1	8	14	15	-10	1	15	15
-6	3	10	10	3	5	31	32	2	8	10	11	-9	1	7	6
-5	3	43	42	6	5	15	15	3	8	5	3	-8	1	13	12
-4	3	38	37	7	5	10	10	4	8	17	17	-7	1	20	20
-2	3	15	16	9	5	16	16	5	8	6	5	-6	1	16	15
-1	3	37	36	10	5	11	11	-14	9	6	6	-5	1	15	15
0	3	25	24	-15	6	5	5	-12	9	10	9	-4	1	31	30
1	3	30	29	-14	6	5	4	-11	9	14	16	-2	1	13	14
2	3	62	61	-13	6	13	12	-10	9	7	8	-1	1	53	54
3	3	29	28	-12	6	10	11	-9	9	5	3	0	1	18	20
4	3	16	14	-9	6	10	9	-8	9	7	8	2	1	23	22
5	3	31	31	-7	6	13	14	-5	9	8	9	3	1	29	25
6	3	7	7	-6	6	25	26	-4	9	8	7	4	1	13	13
11	3	8	8	-5	6	13	13	-2	9	19	20	5	1	23	21
12	3	9	9	-4	6	12	13	-1	9	18	19	6	1	23	23
-16	4	5	6	-3	6	24	23	1	9	17	18	8	1	16	16
-14	4	12	11	-2	6	12	12	2	9	19	19	9	1	24	24
-13	4	13	13	-1	6	7	6	4	9	11	10	10	1	6	6
-11	4	11	10	0	6	9	9	5	9	8	8	12	1	9	8
-10	4	27	27	1	6	9	9	-14	10	7	7	-13	2	14	14
-8	4	20	20	3	6	16	17	-11	10	18	17	-12	2	8	8
-7	4	39	39	4	6	16	16	-10	10	17	17	-10	2	10	8
-6	4	19	17	5	6	5	3	-8	10	12	13	-9	2	19	18
-5	4	20	21	6	6	12	11	-7	10	10	10	-8	2	8	8
-4	4	19	19	7	6	12	13	-5	10	15	15	-7	2	41	41
-3	4	5	6	9	6	5	5	-4	10	22	22	-6	2	38	36
-2	4	12	11	10	6	8	8	-3	10	7	7	-5	2	9	11
-1	4	32	31	-16	7	6	5	-2	10	15	14	-4	2	39	39
0	4	31	31	-15	7	11	11	-1	10	18	17	-3	2	26	25
1	4	22	21	-14	7	5	5	0	10	8	7	-1	2	16	16
2	4	27	26	-13	7	5	6	1	10	5	6	0	2	37	37
3	4	28	27	-12	7	16	17	3	10	6	7	1	2	25	23
4	4	5	5	-11	7	10	10	-14	11	10	10	2	2	12	12
5	4	6	4	-9	7	17	18	-13	11	8	9	3	2	45	44
6	4	5	4	-8	7	5	5	-11	11	12	13	4	2	22	21
8	4	13	13	-6	7	38	37	-10	11	12	12	5	2	5	4
9	4	12	11	-5	7	39	39	-8	11	8	9	6	2	36	34
11	4	6	6	-4	7	10	10	-7	11	13	13	7	2	26	28
12	4	8	8	-3	7	23	23	-6	11	10	9	8	2	5	2
-16	5	6	6	-2	7	15	15	-5	11	8	8	9	2	21	20
-14	5	9	9	-1	7	10	11	-4	11	17	18	10	2	11	11
-13	5	19	18	0	7	12	12	-3	11	9	9	12	2	9	8
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-10	5	21	21	6	7	7	8	-10	12	9	9	-13	3	12	12
-9	5	11	12	-15	8	6	6	-9	12	6	7	-9	3	22	22
-8	5	7	8	-14	8	9	10	-7	12	6	7	-7	3	22	22
-7	5	21	22	-12	8	12	13	-6	12	9	8	-6	3	51	49
-6	5	16	17	-11	8	12	12	-3	12	10	10	-5	3	24	24
-5	5	6	6	-9	8	5	5					-4	3	17	14
-4	5	17	17	-7	8	13	14					-3	3	16	17
-3	5	15	14	-6	8	10	9					-2	3	13	14

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
0	3	33	34	-14	6	14	14	5	8	9	10	-2	1	64	58
1	3	39	39	-13	6	9	9	6	8	5	5	-1	1	46	40
2	3	8	4	-12	6	8	9	-13	9	12	12	0	1	60	51
3	3	24	25	-11	6	11	10	-12	9	17	17	1	1	47	41
4	3	31	29	-8	6	6	6	-10	9	22	23	2	1	40	36
5	3	9	9	-7	6	11	11	-9	9	16	16	3	1	10	13
6	3	15	15	-5	6	42	42	-7	9	6	7	4	1	14	13
7	3	10	11	-4	6	40	40	-6	9	6	7	5	1	16	14
9	3	17	17	-3	6	5	5	-4	9	12	12	6	1	7	7
10	3	11	11	-2	6	23	24	-3	9	21	22	7	1	38	35
12	3	9	9	-1	6	12	12	-2	9	6	7	8	1	33	31
-16	4	5	6	1	6	20	20	-1	9	15	15	9	1	7	8
-15	4	11	11	2	6	24	23	0	9	19	20	10	1	19	18
-13	4	11	12	3	6	8	8	1	9	9	10	11	1	8	7
-12	4	13	14	4	6	24	23	2	9	7	7	13	1	12	11
-11	4	12	12	5	6	24	24	3	9	15	15	-15	2	13	13
-9	4	29	30	6	6	8	8	6	9	7	9	-14	2	10	10
-8	4	23	24	7	6	12	11	-15	10	6	5	-12	2	11	11
-7	4	7	7	8	6	10	10	-13	10	13	12	-10	2	5	4
-6	4	41	41	9	6	6	6	-12	10	15	15	-9	2	13	14
-5	4	26	29	-16	7	7	6	-10	10	17	16	-8	2	26	25
-4	4	11	9	-14	7	14	14	-9	10	18	17	-7	2	8	8
-3	4	14	15	-13	7	8	8	-7	10	9	9	-6	2	35	33
-2	4	16	16	-12	7	5	3	-6	10	17	17	-5	2	44	45
-1	4	14	12	-9	7	4	4	-5	10	7	7	-4	2	14	18
0	4	49	45	-8	7	8	7	-4	10	14	13	-3	2	23	24
1	4	44	41	-7	7	17	17	-3	10	23	22	-2	2	21	17
2	4	11	10	-6	7	19	19	-2	10	7	8	-1	2	8	6
3	4	10	10	-5	7	34	34	0	10	9	9	0	2	21	19
4	4	16	17	-3	7	13	14	4	10	9	9	1	2	23	23
5	4	10	11	-1	7	10	11	-15	11	8	10	2	2	18	16
6	4	5	4	0	7	8	6	-13	11	7	7	3	2	14	13
7	4	7	8	2	7	24	24	-11	11	7	6	4	2	25	24
8	4	10	9	3	7	20	20	-10	11	6	6	5	2	12	14
9	4	10	10	4	7	5	5	-9	11	9	9	7	2	22	22
10	4	16	16	5	7	17	17	-8	11	8	7	8	2	19	19
11	4	12	13	6	7	11	11	-6	11	8	10	10	2	6	6
-15	5	8	8	9	7	9	9	-5	11	14	14	11	2	6	6
-14	5	9	9	-17	8	8	7	-2	11	7	8	13	2	8	7
-12	5	17	17	-16	8	7	8	-11	12	6	6	14	2	5	6
-11	5	21	20	-14	8	11	12	-9	12	5	6	-15	3	9	9
-9	5	14	16	-13	8	14	15	-8	12	8	7	-14	3	15	14
-8	5	12	14	-12	8	6	6	-5	12	7	6	-13	3	8	8
-6	5	11	11	-11	8	10	11	-2	12	8	8	-12	3	6	7
-5	5	11	11	-10	8	21	23					-10	3	17	16
-3	5	8	7	-9	8	6	6		L=-4			-9	3	10	10
-2	5	15	16	-8	8	12	13					-8	3	38	35
0	5	28	27	-7	8	18	18	-15	1	7	8	-7	3	31	30
1	5	17	16	-6	8	12	12	-12	1	12	11	-4	3	30	30
2	5	10	9	-5	8	15	15	-11	1	9	9	-3	3	5	4
3	5	10	10	-4	8	13	14	-9	1	22	22	-2	3	11	14
4	5	5	6	-3	8	19	20	-8	1	24	25	-1	3	23	25
7	5	13	12	-1	8	17	18	-6	1	21	19	1	3	48	45
8	5	9	10	0	8	17	16	-5	1	37	34	2	3	37	37
10	5	6	7	2	8	19	19	-4	1	9	10	4	3	8	8
11	5	12	11	3	8	18	18	-3	1	15	12	5	3	14	14

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
8	3	12	11	-6	6	31	32	-6	9	5	5	-13	2	14	14
9	3	11	11	-4	6	32	31	-5	9	11	11	-12	2	8	8
10	3	6	4	-3	6	28	29	-4	9	5	5	-9	2	9	9
11	3	7	7	-2	6	6	7	-3	9	8	8	-8	2	9	10
12	3	10	9	0	6	23	24	-2	9	19	19	-7	2	15	18
-14	4	14	12	1	6	11	12	-1	9	9	10	-6	2	21	23
-13	4	13	12	2	6	13	13	1	9	12	12	-5	2	17	13
-11	4	13	13	3	6	34	33	2	9	10	10	-3	2	21	19
-10	4	19	19	4	6	19	19	-14	10	9	8	-2	2	21	20
-9	4	9	8	6	6	18	17	-13	10	6	2	-1	2	20	16
-8	4	11	13	7	6	15	15	-11	10	17	15	0	2	21	21
-7	4	19	18	10	6	8	8	-10	10	13	12	1	2	8	11
-6	4	20	16	-16	7	6	7	-8	10	8	8	3	2	49	45
-5	4	4	2	-15	7	12	14	-7	10	7	7	4	2	20	18
-2	4	10	10	-13	7	10	11	-5	10	15	14	5	2	16	15
-1	4	24	24	-12	7	20	21	-4	10	14	14	6	2	50	48
0	4	22	22	-11	7	10	9	-2	10	14	14	7	2	23	21
1	4	36	32	-10	7	11	10	-1	10	8	8	8	2	15	15
2	4	20	19	-9	7	28	29	-14	11	10	10	9	2	22	23
3	4	29	28	-7	7	23	24	-11	11	8	9	10	2	9	8
4	4	8	8	-6	7	53	55	-10	11	6	7	12	2	8	8
6	4	6	6	-5	7	37	38	-8	11	7	6	13	2	7	7
8	4	16	17	-4	7	25	25	-7	11	10	10	-16	3	7	7
9	4	10	11	-3	7	35	35	-5	11	9	9	-15	3	7	8
11	4	6	8	0	7	18	18	-4	11	14	14	-13	3	12	12
12	4	11	12	1	7	9	8	-1	11	9	9	-10	3	6	7
-15	5	7	7	3	7	20	20	-7	12	6	5	-9	3	6	9
-14	5	9	9	4	7	22	21	-6	12	7	6	-8	3	9	8
-13	5	19	19	5	7	8	7	-3	12	10	10	-7	3	8	8
-12	5	8	8	6	7	11	10					-6	3	55	54
-11	5	12	11	7	7	7	7		L=-3			-5	3	28	27
-10	5	10	10	9	7	5	4					-4	3	21	20
-9	5	9	11	-15	8	8	9	-14	1	14	13	-3	3	23	19
-8	5	5	5	-14	8	8	7	-13	1	14	14	-2	3	5	3
-7	5	5	6	-13	8	9	8	-11	1	19	19	-1	3	9	5
-6	5	22	24	-12	8	21	20	-10	1	24	23	0	3	46	43
-5	5	4	3	-11	8	15	14	-8	1	33	32	1	3	51	46
-4	5	11	11	-10	8	7	6	-7	1	30	29	2	3	16	14
-3	5	18	16	-9	8	17	18	-6	1	6	6	3	3	58	58
-2	5	13	10	-8	8	7	7	-5	1	24	23	4	3	45	43
-1	5	23	21	-6	8	20	19	-4	1	13	15	5	3	9	10
0	5	39	40	-5	8	21	20	-3	1	13	9	6	3	33	32
1	5	22	21	-4	8	6	5	-2	1	5	9	7	3	12	11
2	5	27	26	-3	8	9	7	-1	1	59	62	9	3	20	20
3	5	52	50	-2	8	17	17	1	1	33	30	10	3	12	13
5	5	15	14	1	8	12	12	2	1	12	7	12	3	9	9
6	5	22	21	2	8	10	10	3	1	23	15	13	3	7	8
7	5	8	7	4	8	14	14	4	1	43	33	-17	4	6	3
8	5	14	13	5	8	6	3	5	1	4	2	-15	4	13	13
9	5	20	19	-15	9	6	5	7	1	7	6	-14	4	7	7
10	5	13	13	-14	9	7	8	8	1	17	17	-13	4	13	12
-15	6	9	9	-12	9	16	16	9	1	20	20	-12	4	16	15
-13	6	12	13	-11	9	22	23	12	1	6	7	-11	4	13	12
-12	6	9	10	-10	9	6	6	14	1	5	5	-10	4	7	4
-9	6	13	12	-9	9	9	10	15	1	10	9	-9	4	37	34
-7	6	23	23	-8	9	11	12	-16	2	10	10	-8	4	25	24

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-7	4	5	5	2	6	23	23	-9	10	12	12	-2	2	33	26
-6	4	67	63	3	6	7	8	-7	10	7	6	-1	2	25	28
-5	4	23	20	4	6	24	25	-6	10	9	9	0	2	7	12
-4	4	8	12	5	6	25	25	-4	10	12	12	1	2	21	20
-3	4	20	22	6	6	8	8	-3	10	19	18	2	2	34	28
-2	4	8	12	7	6	14	14	-2	10	8	6	3	2	21	21
-1	4	20	16	8	6	10	11	-1	10	5	6	4	2	57	49
0	4	67	61	-17	7	7	7	0	10	13	13	5	2	28	27
1	4	65	63	-15	7	7	7	3	10	7	7	7	2	36	33
2	4	16	16	-14	7	18	18	-13	11	6	5	8	2	29	30
3	4	23	22	-12	7	10	10	-12	11	7	7	10	2	14	13
4	4	30	31	-11	7	10	11	-10	11	7	8	11	2	14	14
5	4	9	7	-9	7	5	5	-9	11	9	8	13	2	11	9
6	4	5	6	-8	7	18	19	-5	11	11	11	14	2	6	7
7	4	14	14	-7	7	18	17	-3	11	9	8	-15	3	10	10
8	4	12	13	-6	7	8	8	-2	11	10	10	-14	3	13	13
9	4	9	10	-5	7	50	49	-11	12	9	7	-13	3	8	7
10	4	19	19	-4	7	36	35	-9	12	11	10	-11	3	7	6
11	4	12	13	-2	7	9	8	-8	12	8	8	-10	3	18	18
12	4	6	4	-1	7	9	8	-6	12	9	8	-9	3	11	10
-14	5	8	7	0	7	6	7	-5	12	9	9	-8	3	44	43
-13	5	5	4	1	7	5	4					-7	3	28	26
-12	5	25	24	3	7	9	8		L=-2			-6	3	22	23
-11	5	24	24	5	7	11	12					-5	3	80	78
-9	5	30	31	-17	8	11	10	-15	1	7	6	-4	3	25	23
-8	5	22	23	-16	8	7	7	-14	1	6	5	-1	3	41	41
-5	5	14	15	-14	8	17	17	-12	1	15	15	0	3	7	6
-4	5	11	11	-13	8	16	16	-9	1	21	22	1	3	68	72
-3	5	15	16	-11	8	19	18	-8	1	14	17	2	3	55	59
-2	5	23	26	-10	8	21	21	-7	1	11	11	3	3	11	12
0	5	31	30	-8	8	13	12	-6	1	7	7	4	3	15	15
1	5	29	29	-7	8	17	16	-5	1	32	31	5	3	33	32
2	5	19	19	-6	8	11	12	-4	1	20	16	6	3	16	17
3	5	10	10	-5	8	17	15	-2	1	30	38	8	3	24	25
4	5	12	12	-4	8	15	15	1	1	8	15	9	3	18	18
7	5	18	17	-3	8	16	15	2	1	51	51	10	3	10	9
8	5	11	12	-1	8	12	12	3	1	12	9	11	3	11	12
10	5	11	12	0	8	6	6	4	1	23	20	12	3	7	8
11	5	9	9	1	8	6	4	5	1	10	12	-17	4	5	7
-15	6	6	7	2	8	12	12	6	1	24	25	-15	4	5	4
-14	6	14	15	3	8	8	9	7	1	42	41	-14	4	14	14
-13	6	6	6	5	8	8	7	8	1	20	21	-13	4	8	10
-12	6	13	13	-13	9	10	10	9	1	13	14	-12	4	6	5
-11	6	18	18	-12	9	9	9	10	1	18	17	-11	4	21	20
-10	6	8	9	-10	9	14	14	11	1	8	8	-10	4	24	26
-9	6	6	6	-9	9	10	10	13	1	14	12	-9	4	14	14
-8	6	21	21	-4	9	7	7	-15	2	10	14	-8	4	38	36
-7	6	15	15	-3	9	12	12	-14	2	13	14	-7	4	36	37
-6	6	9	10	-1	9	12	12	-12	2	14	14	-6	4	10	8
-5	6	60	59	0	9	13	12	-10	2	6	6	-5	4	40	38
-4	6	49	46	1	9	5	4	-9	2	13	13	-4	4	35	42
-3	6	14	13	2	9	10	9	-8	2	28	28	-3	4	19	20
-2	6	36	35	3	9	9	10	-6	2	57	59	-2	4	44	43
-1	6	17	18	-13	10	9	8	-5	2	54	55	-1	4	70	67
0	6	5	4	-12	10	8	9	-4	2	17	16	0	4	33	29
1	6	24	23	-10	10	12	11	-3	2	50	49	1	4	59	56

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
2	4	37	35	-9	7	13	13	-10	11	7	7	-15	3	7	7
3	4	34	32	-7	7	13	11	-8	11	9	9	-13	3	22	21
4	4	11	11	-5	7	26	26	-7	11	13	12	-12	3	6	7
5	4	6	5	-4	7	22	22	-5	11	14	13	-11	3	8	8
9	4	8	8	-3	7	18	20	-4	11	15	15	-10	3	6	8
11	4	11	11	-2	7	15	15	-2	11	6	6	-9	3	21	20
12	4	8	8	-1	7	6	7	-1	11	10	9	-8	3	26	26
-17	5	6	6	0	7	9	10					-7	3	38	38
-14	5	16	17	1	7	6	6		L=-1			-6	3	73	78
-13	5	21	22	3	7	22	22					-5	3	12	17
-12	5	6	5	4	7	17	17	-16	1	7	8	-4	3	58	57
-11	5	23	25	6	7	10	11	-14	1	10	11	-3	3	58	55
-10	5	23	24	-15	8	8	7	-13	1	10	10	-1	3	52	47
-9	5	14	14	-13	8	9	8	-11	1	13	14	0	3	60	58
-8	5	8	9	-12	8	11	11	-10	1	21	21	1	3	16	12
-7	5	20	22	-11	8	7	7	-9	1	7	8	2	3	52	47
-6	5	31	31	-10	8	6	6	-8	1	39	39	3	3	45	48
-5	5	5	6	-9	8	10	10	-7	1	46	44	4	3	19	21
-4	5	30	31	-6	8	12	12	-6	1	11	9	5	3	19	19
-3	5	29	28	-5	8	9	7	-5	1	53	50	6	3	21	21
-1	5	33	33	-2	8	13	13	-4	1	27	26	8	3	5	2
0	5	31	29	1	8	16	15	-3	1	8	9	9	3	13	14
1	5	10	7	2	8	7	7	-2	1	26	22	10	3	6	5
2	5	22	22	3	8	9	9	2	1	58	60	12	3	8	7
3	5	29	29	4	8	14	15	3	1	23	25	13	3	6	5
6	5	7	8	7	8	7	6	4	1	23	28	-16	4	7	7
8	5	12	11	-14	9	5	7	5	1	7	10	-15	4	14	14
9	5	10	11	-12	9	11	12	6	1	26	26	-13	4	23	23
10	5	6	6	-11	9	23	22	8	1	30	30	-12	4	20	21
-17	6	8	7	-10	9	5	5	9	1	36	36	-10	4	21	21
-16	6	8	7	-9	9	14	13	11	1	10	9	-9	4	32	31
-15	6	7	6	-8	9	12	12	12	1	12	11	-7	4	19	18
-14	6	14	14	-5	9	8	8	14	1	8	8	-6	4	52	50
-13	6	22	22	-4	9	5	4	15	1	7	8	-5	4	7	8
-12	6	10	9	-3	9	7	8	-17	2	7	7	-4	4	10	10
-11	6	9	10	-2	9	19	20	-16	2	9	10	-3	4	8	11
-10	6	7	7	-1	9	10	9	-12	2	6	7	-1	4	14	10
-9	6	9	8	0	9	6	5	-9	2	18	19	0	4	49	45
-8	6	8	8	1	9	14	14	-8	2	18	18	1	4	35	35
-7	6	21	19	2	9	11	10	-7	2	41	43	2	4	7	7
-6	6	26	24	4	9	9	9	-6	2	44	45	3	4	12	12
-5	6	5	3	-14	10	9	8	-4	2	37	38	4	4	15	14
-4	6	38	35	-12	10	7	6	-3	2	63	70	5	4	12	13
-3	6	18	19	-11	10	18	17	-2	2	17	20	6	4	9	10
-2	6	8	9	-10	10	9	8	1	2	21	15	9	4	7	7
-1	6	5	7	-9	10	8	7	2	2	37	41	10	4	10	11
0	6	5	6	-8	10	10	9	3	2	58	53	11	4	8	8
1	6	8	7	-5	10	17	16	4	2	9	7	-16	5	5	4
2	6	14	14	-4	10	12	11	5	2	22	22	-15	5	12	12
3	6	18	18	-3	10	9	8	6	2	49	49	-14	5	6	5
5	6	9	10	-2	10	16	16	7	2	18	16	-13	5	13	13
6	6	11	11	-1	10	8	7	8	2	22	20	-12	5	29	29
-16	7	8	7	1	10	5	6	9	2	22	22	-11	5	15	14
-15	7	14	14	2	10	5	3	12	2	8	7	-10	5	9	9
-13	7	14	14	-12	11	5	5	-17	3	7	8	-9	5	19	21
-12	7	15	15	-11	11	11	12	-16	3	12	13	-8	5	9	11

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-7	5	9	9	-11	8	19	19	-15	1	8	8	-1	3	4	6
-6	5	17	15	-10	8	20	20	-13	1	9	9	0	3	7	7
-5	5	9	9	-8	8	17	16	-12	1	22	23	1	3	47	46
-4	5	9	7	-7	8	16	16	-10	1	20	21	2	3	31	33
-3	5	4	3	-6	8	7	6	-9	1	39	40	4	3	24	23
-2	5	12	12	-5	8	19	18	-7	1	23	22	5	3	24	22
0	5	15	14	-4	8	21	20	-6	1	40	33	7	3	8	8
1	5	21	21	-3	8	13	13	-5	1	22	27	8	3	15	15
2	5	14	14	-1	8	19	17	-4	1	8	8	9	3	6	4
3	5	14	14	0	8	7	7	-3	1	42	36	10	3	11	11
4	5	13	13	1	8	5	4	-1	1	16	14	11	3	8	8
6	5	6	7	2	8	13	13	1	1	20	21	-17	4	5	5
7	5	15	14	3	8	12	12	2	1	33	32	-14	4	16	16
9	5	7	7	5	8	8	8	6	1	13	15	-13	4	8	9
10	5	11	10	-12	9	5	5	7	1	24	23	-12	4	5	5
11	5	6	6	-11	9	10	10	8	1	5	5	-11	4	16	16
-14	6	12	13	-10	9	17	17	9	1	14	13	-10	4	17	18
-12	6	8	9	-9	9	11	8	10	1	7	5	-9	4	10	9
-11	6	11	11	-7	9	9	9	13	1	8	8	-8	4	30	29
-10	6	11	12	-6	9	8	8	-16	2	9	9	-7	4	25	27
-9	6	7	7	-4	9	16	16	-15	2	22	21	-5	4	39	37
-8	6	12	12	-3	9	13	13	-14	2	13	12	-4	4	10	13
-7	6	12	13	-1	9	14	13	-13	2	8	9	-2	4	21	21
-5	6	39	37	0	9	8	10	-12	2	28	29	-1	4	31	31
-4	6	26	23	2	9	8	8	-10	2	7	9	0	4	13	12
-3	6	8	8	3	9	8	7	-9	2	28	30	1	4	47	46
-2	6	12	13	-14	10	6	5	-8	2	25	25	2	4	32	31
-1	6	10	11	-13	10	13	12	-7	2	14	14	3	4	21	21
1	6	17	19	-12	10	7	8	-6	2	56	61	4	4	19	20
2	6	18	18	-10	10	15	13	-5	2	54	54	5	4	8	8
4	6	25	26	-9	10	13	12	-3	2	26	27	8	4	18	19
5	6	19	20	-7	10	10	9	-2	2	31	26	9	4	7	8
7	6	16	16	-6	10	12	11	-1	2	11	11	11	4	12	12
8	6	10	11	-4	10	14	14	0	2	9	8	12	4	9	7
-17	7	6	7	-3	10	16	15	1	2	5	7	-14	5	12	12
-15	7	5	5	-1	10	6	7	2	2	18	21	-13	5	13	13
-14	7	12	13	0	10	9	9	3	2	16	13	-12	5	6	5
-11	7	9	8	-10	11	8	8	4	2	38	37	-11	5	15	14
-10	7	5	4	-6	11	8	6	5	2	13	13	-10	5	16	16
-9	7	8	7	-5	11	7	6	6	2	10	11	-9	5	13	13
-8	7	18	19	-3	11	7	6	7	2	29	28	-8	5	10	11
-7	7	5	4					8	2	10	11	-7	5	14	15
-5	7	41	41		L= 0			9	2	4	4	-6	5	8	7
-4	7	16	16					10	2	10	10	-5	5	13	14
-3	7	7	6	-5	0	20	26	11	2	5	4	-4	5	13	12
-2	7	11	11	3	0	90	86	13	2	9	9	-3	5	8	8
-1	7	7	8	5	0	20	26	-15	3	12	13	-1	5	20	20
0	7	10	9	6	0	25	28	-13	3	5	4	0	5	18	19
1	7	11	10	7	0	33	32	-12	3	8	9	2	5	18	18
2	7	14	14	9	0	38	38	-10	3	12	12	3	5	21	21
4	7	8	8	10	0	21	21	-9	3	8	9	6	5	12	12
5	7	16	16	12	0	6	6	-8	3	25	27	8	5	13	12
6	7	7	8	13	0	6	6	-5	3	57	54	9	5	15	14
-16	8	5	4	15	0	6	5	-4	3	10	11	10	5	6	5
-14	8	10	10	16	0	5	5	-3	3	21	17	-17	6	7	7
-13	8	13	13	-16	1	6	6	-2	3	6	10	-16	6	5	4

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-14	6	10	10	0	8	9	9	-5	1	53	50	5	3	14	14
-13	6	15	16	1	8	13	12	-4	1	25	26	6	3	18	18
-12	6	11	10	3	8	9	10	-3	1	5	4	7	3	11	11
-11	6	7	6	4	8	8	9	-2	1	23	25	9	3	21	21
-10	6	11	11	-15	9	6	5	0	1	26	28	10	3	12	12
-9	6	11	10	-14	9	6	5	1	1	18	22	12	3	10	11
-8	6	10	10	-12	9	15	14	2	1	36	36	-16	4	6	4
-7	6	20	20	-11	9	16	16	3	1	22	24	-15	4	7	8
-6	6	20	19	-9	9	16	15	4	1	21	22	-13	4	11	10
-5	6	7	7	-8	9	12	11	5	1	10	10	-12	4	10	11
-4	6	42	41	-5	9	7	7	6	1	9	8	-10	4	13	12
-3	6	24	24	-2	9	14	13	7	1	13	14	-9	4	19	20
-2	6	12	12	1	9	9	9	8	1	28	27	-8	4	4	4
-1	6	19	20	-12	10	6	7	9	1	17	16	-7	4	18	19
0	6	10	11	-11	10	13	12	10	1	10	10	-6	4	33	30
1	6	9	10	-9	10	8	7	11	1	7	7	-4	4	6	9
2	6	15	15	-8	10	6	5	12	1	5	4	-3	4	16	17
3	6	17	17	-5	10	7	8	14	1	7	7	-2	4	10	13
4	6	6	5	-4	10	6	4	-17	2	7	7	-1	4	9	9
5	6	9	9	-3	10	7	6	-16	2	8	8	0	4	53	54
6	6	14	15	-2	10	8	8	-14	2	9	11	1	4	22	24
7	6	6	7					-13	2	12	13	2	4	8	8
8	6	6	5		L= 1			-9	2	17	18	3	4	20	20
9	6	5	6					-8	2	15	16	4	4	18	19
-15	7	10	10	-15	0	6	7	-7	2	34	37	5	4	5	4
-13	7	14	15	-14	0	11	10	-6	2	34	32	7	4	13	13
-12	7	13	13	-12	0	17	17	-5	2	8	9	8	4	5	6
-10	7	8	7	-11	0	20	19	-4	2	24	23	9	4	10	10
-9	7	12	12	-9	0	32	33	-3	2	12	10	10	4	12	12
-7	7	10	11	-8	0	32	31	-1	2	26	20	11	4	8	7
-6	7	38	38	-6	0	11	12	1	2	10	12	-16	5	6	3
-5	7	22	22	-5	0	12	8	2	2	11	10	-15	5	8	8
-4	7	29	30	-3	0	58	59	3	2	22	19	-14	5	5	5
-3	7	29	28	-2	0	18	19	4	2	5	6	-13	5	12	12
-2	7	13	12	0	0	7	6	5	2	16	16	-12	5	25	27
-1	7	15	15	2	0	11	18	6	2	25	26	-11	5	10	11
0	7	15	14	3	0	55	60	8	2	16	17	-10	5	13	14
1	7	7	6	4	0	11	9	9	2	16	16	-9	5	19	21
2	7	6	5	5	0	10	8	11	2	6	7	-8	5	9	10
3	7	21	21	6	0	5	2	12	2	7	8	-7	5	10	9
4	7	15	15	7	0	18	18	-16	3	11	12	-6	5	25	26
5	7	5	2	8	0	24	22	-15	3	6	6	-5	5	29	30
6	7	9	10	9	0	10	11	-14	3	5	6	-3	5	36	35
-16	8	8	7	10	0	8	9	-13	3	15	15	-2	5	37	37
-15	8	8	8	11	0	11	11	-9	3	19	20	0	5	33	31
-13	8	17	16	12	0	6	6	-7	3	30	30	1	5	30	29
-12	8	14	12	14	0	7	7	-6	3	51	52	2	5	10	10
-10	8	14	14	-15	1	7	7	-5	3	5	5	3	5	19	19
-9	8	14	14	-14	1	13	14	-4	3	34	33	4	5	19	18
-8	8	9	2	-13	1	12	12	-3	3	4	7	6	5	9	9
-7	8	7	7	-12	1	6	7	-2	3	11	11	9	5	8	6
-6	8	22	20	-11	1	20	22	-1	3	18	20	10	5	7	7
-5	8	10	9	-10	1	21	22	0	3	28	27	-15	6	10	10
-4	8	5	5	-8	1	43	45	2	3	43	44	-14	6	12	12
-3	8	11	10	-7	1	42	43	3	3	32	32	-13	6	7	7
-2	8	13	13	-6	1	10	10	4	3	15	15	-12	6	18	18

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-11	6	10	9		L= 2			-8	2	22	22	-4	4	21	21
-9	6	5	1					-7	2	7	7	-3	4	11	11
-8	6	15	15	-16	0	7	6	-6	2	37	38	-2	4	30	29
-7	6	8	8	-15	0	6	5	-5	2	45	44	-1	4	30	30
-6	6	14	13	-13	0	7	8	-4	2	12	13	0	4	6	5
-5	6	42	40	-12	0	8	8	-3	2	19	17	1	4	39	39
-4	6	15	15	-10	0	20	20	-2	2	25	21	2	4	33	33
-3	6	19	19	-9	0	34	33	-1	2	14	13	3	4	16	17
-2	6	16	17	-8	0	6	6	0	2	31	25	4	4	22	23
-1	6	10	10	-7	0	29	28	1	2	43	43	5	4	11	11
1	6	16	16	-6	0	22	23	2	2	10	12	8	4	10	11
2	6	13	12	-5	0	18	17	3	2	27	27	11	4	8	8
4	6	20	19	-4	0	5	11	4	2	36	37	-14	5	19	19
5	6	9	9	-3	0	31	29	5	2	16	16	-13	5	11	10
7	6	9	9	-2	0	7	4	6	2	9	9	-12	5	9	9
-15	7	11	13	-1	0	39	44	7	2	31	31	-11	5	21	22
-14	7	16	16	1	0	12	7	8	2	15	15	-10	5	11	11
-12	7	15	16	2	0	21	27	9	2	6	5	-8	5	18	20
-11	7	12	13	3	0	23	23	10	2	15	14	-7	5	13	15
-9	7	13	13	4	0	13	9	11	2	5	6	-5	5	21	22
-8	7	20	19	5	0	16	17	13	2	8	8	-4	5	11	11
-6	7	13	12	6	0	4	6	-15	3	9	9	-1	5	13	13
-5	7	33	32	7	0	15	16	-14	3	10	12	0	5	15	16
-4	7	6	6	8	0	6	7	-13	3	5	4	2	5	14	15
-3	7	9	7	9	0	29	29	-12	3	9	8	3	5	14	12
0	7	7	7	10	0	20	21	-10	3	8	8	8	5	6	8
1	7	8	8	12	0	8	8	-9	3	14	14	9	5	6	5
2	7	10	9	13	0	8	8	-8	3	22	22	-16	6	6	5
4	7	9	9	15	0	5	5	-7	3	7	6	-14	6	15	14
5	7	8	8	-16	1	8	8	-6	3	12	13	-13	6	17	17
-14	8	9	9	-15	1	9	8	-5	3	53	55	-12	6	6	5
-13	8	7	8	-13	1	7	9	-4	3	22	23	-11	6	10	10
-11	8	17	16	-12	1	12	13	-3	3	6	5	-10	6	16	15
-10	8	13	13	-10	1	7	8	-2	3	35	34	-9	6	10	10
-9	8	9	6	-9	1	20	20	-1	3	15	14	-8	6	12	11
-8	8	13	12	-7	1	13	14	0	3	24	25	-7	6	20	20
-7	8	7	8	-6	1	17	15	1	3	56	59	-6	6	11	11
-5	8	9	10	-4	1	16	17	2	3	21	22	-5	6	10	9
-4	8	9	8	-3	1	5	3	3	3	12	14	-4	6	30	29
-3	8	7	7	-2	1	3	4	4	3	30	31	-3	6	12	12
-1	8	9	9	-1	1	15	17	5	3	20	22	-2	6	6	6
2	8	9	9	0	1	34	40	6	3	8	9	-1	6	10	10
3	8	7	6	2	1	13	15	7	3	11	11	0	6	5	5
-13	9	7	8	6	1	6	6	8	3	11	11	1	6	8	7
-11	9	8	8	7	1	25	24	10	3	7	8	2	6	7	8
-10	9	12	13	8	1	12	13	-17	4	6	6	3	6	8	7
-8	9	7	4	9	1	12	13	-14	4	19	20	5	6	9	8
-4	9	7	8	10	1	16	16	-13	4	7	7	6	6	10	9
-3	9	6	5	11	1	5	6	-12	4	15	15	-15	7	6	5
-1	9	7	8	13	1	11	10	-11	4	22	23	-13	7	11	11
-10	10	10	9	-16	2	9	9	-10	4	7	7	-12	7	8	9
-9	10	6	6	-15	2	16	16	-9	4	22	22	-9	7	7	8
-4	10	10	10	-14	2	6	6	-8	4	31	30	-7	7	6	5
-3	10	8	8	-13	2	5	5	-7	4	20	19	-6	7	17	18
				-12	2	14	14	-6	4	14	14	-5	7	8	7
				-9	2	14	14	-5	4	46	45	-4	7	18	18

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-3	7	8	9	3	1	17	19	-12	4	9	9	-5	9	8	5
-1	7	8	7	4	1	21	23	-10	4	17	17	-4	9	9	8
3	7	11	11	5	1	22	25	-9	4	20	21				
4	7	7	7	6	1	13	14	-8	4	7	7		L= 4		
-13	8	7	8	7	1	14	16	-7	4	28	28				
-12	8	7	7	8	1	28	29	-6	4	26	24	-15	0	6	5
-10	8	10	9	9	1	10	11	-5	4	7	7	-13	0	8	8
-9	8	7	8	10	1	7	8	-4	4	14	14	-12	0	10	10
-7	8	5	5	14	1	6	5	-3	4	7	5	-11	0	6	4
-6	8	10	11	-16	2	6	5	-1	4	9	8	-10	0	23	23
-4	8	6	6	-15	2	6	4	0	4	30	28	-9	0	18	18
-3	8	7	7	-14	2	14	14	1	4	5	5	-8	0	13	13
-1	8	5	4	-13	2	14	15	2	4	12	11	-7	0	27	26
0	8	7	7	-12	2	5	4	3	4	12	11	-6	0	11	11
3	8	8	8	-11	2	15	16	4	4	5	4	-5	0	6	7
-12	9	9	9	-10	2	4	1	5	4	7	7	-4	0	17	17
-11	9	9	9	-8	2	31	31	7	4	5	5	-3	0	24	24
-9	9	9	9	-7	2	28	28	9	4	9	9	-2	0	10	7
-8	9	7	6	-6	2	9	10	-13	5	10	11	-1	0	48	44
-6	9	7	6	-5	2	29	29	-12	5	19	19	0	0	89	94
-5	9	9	7	-4	2	41	41	-11	5	8	8	1	0	4	1
-3	9	8	9	-3	2	5	7	-10	5	9	10	2	0	10	14
-2	9	10	11	-2	2	21	20	-9	5	15	16	3	0	35	34
				-1	2	8	11	-7	5	9	9	4	0	23	21
	L= 3			0	2	9	9	-6	5	16	17	5	0	13	14
				2	2	22	21	-5	5	14	15	6	0	25	25
-15	0	7	7	3	2	29	29	-4	5	6	6	7	0	17	17
-14	0	8	8	5	2	23	23	-3	5	19	20	8	0	14	13
-12	0	7	6	6	2	22	22	-2	5	15	16	9	0	26	26
-11	0	10	10	8	2	15	14	-1	5	6	6	10	0	14	14
-9	0	17	17	9	2	8	8	0	5	16	16	12	0	7	7
-8	0	23	22	-16	3	10	12	1	5	10	9	13	0	7	8
-5	0	13	10	-14	3	11	14	3	5	9	10	-15	1	8	7
-4	0	5	5	-13	3	20	21	4	5	6	7	-14	1	7	6
-3	0	21	25	-11	3	9	9	7	5	8	9	-13	1	15	14
-2	0	21	24	-10	3	8	8	-15	6	6	5	-12	1	15	13
-1	0	67	66	-9	3	16	16	-14	6	7	6	-11	1	11	12
0	0	33	33	-8	3	21	22	-13	6	5	6	-10	1	17	18
1	0	102	103	-7	3	36	38	-12	6	11	10	-9	1	19	18
2	0	24	23	-6	3	38	40	-8	6	6	5	-8	1	5	7
4	0	31	36	-5	3	14	15	-5	6	21	21	-7	1	30	29
6	0	7	8	-4	3	35	35	-4	6	5	4	-6	1	33	32
-11	1	17	19	-3	3	5	6	-3	6	14	14	-4	1	44	40
-10	1	16	17	-2	3	5	3	-2	6	7	7	-3	1	22	23
-9	1	5	5	-1	3	5	7	4	6	10	10	-1	1	24	24
-8	1	36	39	0	3	23	24	5	6	5	5	0	1	33	34
-7	1	21	22	1	3	8	8	-14	7	11	11	1	1	19	21
-6	1	6	2	2	3	28	30	-12	7	10	10	2	1	9	9
-5	1	39	40	3	3	27	27	-11	7	8	8	3	1	19	19
-4	1	29	30	4	3	8	9	-9	7	7	6	4	1	14	15
-3	1	6	4	5	3	15	15	-8	7	8	9	5	1	6	5
-2	1	54	55	6	3	10	9	-5	7	22	22	6	1	14	13
-1	1	86	85	9	3	13	13	-3	7	10	9	7	1	16	16
0	1	6	8	-16	4	8	8	4	7	10	10	9	1	12	13
1	1	56	54	-15	4	6	5	-8	9	8	8	10	1	10	10
2	1	47	48	-13	4	14	14	-7	9	8	7	13	1	7	5

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-15	2	14	14	-14	5	11	11	4	1	5	6	-8	7	9	9
-13	2	11	11	-11	5	11	11	6	1	6	4	-6	7	8	8
-12	2	15	15	-8	5	6	6	7	1	6	6	-5	7	15	16
-9	2	21	21	-5	5	9	10	8	1	16	17	-3	7	8	8
-8	2	26	26	-4	5	9	9	9	1	5	5	-2	7	7	7
-7	2	17	18	-2	5	7	7	10	1	8	7				
-6	2	47	47	-1	5	12	12	-15	2	10	9		L= 6		
-5	2	34	35	0	5	5	5	-14	2	13	13				
-4	2	8	8	1	5	6	6	-13	2	6	7	-14	0	6	6
-3	2	25	25	2	5	14	14	-12	2	8	7	-13	0	7	6
-2	2	14	16	3	5	7	6	-11	2	9	9	-12	0	6	4
-1	2	4	3	4	5	7	7	-8	2	14	14	-11	0	6	6
0	2	17	19	5	5	7	6	-7	2	9	8	-10	0	14	15
1	2	23	24	-10	7	6	7	-6	2	5	4	-9	0	7	7
3	2	18	18	-9	7	6	5	-5	2	8	7	-8	0	11	11
4	2	12	11	-7	7	9	9	-4	2	18	18	-7	0	8	9
6	2	6	5	-6	7	11	12	-3	2	5	7	-5	0	17	16
7	2	13	13	-4	7	15	15	-2	2	5	6	-4	0	6	4
8	2	4	4	-3	7	5	6	1	2	6	6	-3	0	12	10
9	2	7	6	-1	7	6	6	2	2	11	12	-2	0	9	7
10	2	8	8	0	7	7	7	3	2	10	10	-1	0	17	18
-15	3	10	11					5	2	13	14	0	0	43	43
-14	3	6	6		L= 5			6	2	11	11	1	0	5	5
-12	3	9	9					7	2	6	5	2	0	9	9
-10	3	5	6	-15	0	11	11	8	2	12	11	3	0	11	11
-9	3	16	16	-14	0	8	8	9	2	5	5	4	0	6	6
-8	3	19	20	-12	0	12	12	-14	3	8	8	5	0	9	10
-6	3	15	16	-11	0	12	12	-13	3	13	14	6	0	12	11
-5	3	31	32	-9	0	25	24	-9	3	8	9	7	0	5	4
-3	3	6	6	-8	0	36	36	-8	3	9	10	8	0	14	14
-2	3	10	11	-7	0	4	4	-7	3	15	15	9	0	18	17
0	3	17	19	-6	0	26	26	-6	3	20	20	12	0	6	4
1	3	22	24	-5	0	27	26	-4	3	16	16	-13	1	11	11
2	3	5	5	-3	0	40	38	-3	3	6	5	-12	1	11	12
3	3	11	12	-2	0	28	28	-1	3	7	7	-11	1	6	6
4	3	9	9	-1	0	25	24	0	3	15	15	-10	1	11	11
6	3	6	7	0	0	39	39	2	3	23	23	-9	1	7	8
8	3	6	5	1	0	65	62	3	3	15	17	-8	1	5	6
10	3	6	7	3	0	16	16	5	3	15	15	-7	1	14	14
-14	4	12	13	4	0	18	18	6	3	6	7	-6	1	11	11
-12	4	8	8	5	0	17	16	9	3	9	9	-4	1	15	17
-11	4	12	12	6	0	13	13	-13	5	10	10	-3	1	9	10
-9	4	10	10	7	0	8	8	-12	5	12	13	-1	1	17	18
-8	4	12	11	8	0	11	10	-10	5	9	10	0	1	21	20
-7	4	6	7	10	0	12	12	-9	5	9	10	1	1	6	5
-5	4	17	17	11	0	7	7	-7	5	12	12	3	1	15	16
-4	4	8	8	-14	1	8	10	-6	5	16	16	4	1	7	8
-2	4	11	10	-12	1	6	6	-5	5	5	6	5	1	10	10
-1	4	12	12	-11	1	14	15	-4	5	11	11	6	1	11	15
0	4	4	4	-10	1	8	9	-3	5	16	17	7	1	9	10
1	4	22	21	-4	1	12	11	-2	5	10	10	9	1	10	12
2	4	13	13	-2	1	24	25	0	5	13	14	10	1	6	6
3	4	5	5	-1	1	33	34	1	5	13	13	-13	2	6	6
4	4	14	14	0	1	7	7	3	5	12	13	-12	2	11	11
5	4	6	6	1	1	24	27	4	5	10	9	-9	2	10	10
8	4	11	10	2	1	8	9	-9	7	11	11	-8	2	11	10

Table 9. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-7	2	15	14	-11	0	12	11	-11	3	7	5	6	1	6	5
-6	2	23	24	-9	0	17	17	-10	3	8	7	-9	3	7	9
-5	2	13	14	-8	0	22	21	-9	3	6	5	-8	3	6	4
-4	2	11	11	-6	0	17	16	-8	3	15	16	-6	3	8	9
-3	2	17	17	-5	0	13	13	-7	3	18	18	-5	3	11	12
-12	3	9	8	-4	0	5	4	-6	3	9	9	1	3	9	9
-9	3	12	14	-3	0	21	22	-5	3	11	12	4	3	9	9
-8	3	15	14	-2	0	11	9	-4	3	16	18				
-6	3	19	21	-1	0	5	5	-2	3	6	4		L= 9		
-5	3	22	23	0	0	28	25	-1	3	11	11				
-4	3	5	5	1	0	32	30	0	3	7	9	-9	1	6	8
-3	3	12	13	3	0	7	7	1	3	8	8	-8	1	7	8
-2	3	6	8	4	0	16	15	2	3	14	15	-5	1	7	8
0	3	12	12	6	0	9	8	5	3	6	6	-4	1	6	4
1	3	19	21	7	0	11	11	-6	5	6	6	-2	1	8	9
2	3	6	3	8	0	12	11	-3	5	6	7	4	1	7	6
3	3	9	9	10	0	12	11	-2	5	6	4	-5	3	8	9
4	3	14	15	11	0	9	8								
5	3	6	7	-11	1	8	8		L= 8				L=10		
6	3	6	6	-9	1	7	4								
7	3	6	6	-8	1	15	16	-11	1	7	9	-7	1	9	10
-12	5	8	8	-6	1	9	9	-10	1	12	12	-4	1	9	9
-11	5	12	13	-5	1	17	18	-9	1	8	7	-1	1	7	7
-9	5	7	7	-3	1	10	9	-8	1	7	8	0	1	8	5
-6	5	8	6	-2	1	19	19	-7	1	18	20				
-5	5	13	13	-1	1	17	16	-6	1	11	12				
-4	5	9	9	0	1	7	7	-5	1	7	6				
-2	5	10	11	1	1	17	19	-4	1	19	19				
-1	5	9	9	2	1	13	13	-3	1	12	12				
1	5	7	7	4	1	10	11	-1	1	18	20				
				5	1	11	11	0	1	17	19				
	L= 7			7	1	8	9	2	1	10	11				
				8	1	16	16	3	1	8	9				
-12	0	7	8	10	1	6	6	5	1	6	6				

tioned such that the long dimension was parallel to the glass fiber. Precession photographs indicated a triclinic crystal P1 or $P\bar{1}$. Space group $P\bar{1}$ was assumed and the successful refinement of the structure later confirmed this assumption.

The crystal was transferred to an automated Picker four-angle diffractometer and 22 reflections were used to refine cell parameters by a least-squares procedure. The cell parameters obtained were: $a = 9.524(1)$Å, $b = 11.402(3)$Å, $c = 15.880(2)$Å, $\alpha = 107.16(1)^\circ$, $\beta = 140.63(1)^\circ$, $\gamma = 80.66(2)^\circ$ and $V = 1038.98$Å^3 (25°C, molybdenum radiation, $\lambda = 0.7107$Å). A Delaunay reduction using these cell parameters confirmed the triclinic description of the unit cell. The conventional reduced cell parameters obtained were: $a' = 9.524(1)$Å, $b' = 12.938$Å, $c' = 11.402$Å, $\alpha' = 129.669^\circ$, $\beta' = 99.336^\circ$ and $\gamma' = 94.004^\circ$. The transformation matrix is:

$$\begin{bmatrix} a' \\ b' \\ c' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 1 & 1 & 1 \\ 0 & -1 & 0 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

The calculated density of 1.55 g-cm^{-3} based on two formula units per unit cell, agreed well with the observed density of 1.56(1) g-cm^{-3} measured by the flotation method using a mixture of n-heptane and carbon tetrachloride.

Intensity measurements were made in the same way as in the previous structure. A standard reflection of indices 0,4,2 was monitored every 50 reflections and showed no significant variation throughout the

entire data collection. Of a total of 2498 reflections collected, only 1013 were unique and nonzero. The basis for accepting the reflections was that $\sigma(I)/I$ be less than 0.30. The ignorance factor, p, used in the calculation of $\sigma(I)$ was set at 0.02. Intensities were corrected for background and Lorentz polarization as was done previously. The linear absorption coefficient, $\mu = 18.18\ cm^{-1}$, was not considered large enough to necessitate making absorption corrections. Since density measurements indicated that there were two dimeric units per unit cell, each dimer unit would have to occupy an inversion center if each half of the dimer were asymmetric. There were, then, two independent asymmetric units to be located in order to completely describe the structure.

Positions for the nickel atoms were found from a three-dimensional Patterson function using 806 of the strongest unique reflections. A structure factor calculation using all 1013 unique nonzero reflections, phased on the nickel coordinates of the two asymmetric units, revealed the positions of all 26 of the remaining non-hydrogen atoms. Full-matrix least-squares refinement of these coordinates, the scale factor, and the isotropic temperature factors dropped the conventional R_1 value to 0.096 from an initial value of 0.34 with only the nickel atoms included. After applying anisotropic temperature factors to the nickel atoms, employing a weighting scheme as previously defined, and refining by least-squares, the residuals, R_1 and R_2, settled down to the values of 0.0741 and 0.0757 respectively. The positional and thermal parameters from the last cycle of least-squares refinement are presented in Table 10. The observed and calculated structure factors for all 1013 unique nonzero reflections are given in Table 11.

Table 10. Final Positional and Thermal Parameters for $[Ni(H\cdot DIIMINE)]_2$

Atom	x	y	z	B^a, $Å^2$
UNIT 1				
Ni	0.1465(7)	0.1639(4)	0.0009(5)	3.0(1)[b]
O1	0.084(3)	-0.007(1)	-0.067(1)	5.4(6)
O2	0.098(2)	0.157(1)	0.095(1)	4.7(5)
N1	0.205(2)	0.156(1)	-0.088(1)	2.7(4)
N2	0.210(2)	0.330(1)	0.074(1)	2.5(5)
C1	0.256(2)	0.253(1)	-0.093(1)	2.0(7)
C2	0.278(4)	0.235(2)	-0.182(2)	5.8(9)
C3	0.294(3)	0.368(2)	-0.020(2)	2.3(6)
C4	0.276(2)	0.415(1)	0.062(1)	2.5(6)
C5	0.349(3)	0.549(1)	0.146(2)	3.2(7)
C6	0.149(2)	0.029(1)	-0.179(1)	2.9(7)
C7	0.143(4)	-0.054(2)	-0.128(2)	5.7(8)
C8	0.200(2)	0.379(1)	0.169(2)	3.0(6)
C9	0.053(3)	0.276(2)	0.122(2)	4.1(8)
UNIT 2				
Ni	0.1361(6)	0.1654(4)	0.4962(4)	2.80(9)[c]
O1	-0.130(2)	0.114(1)	0.417(1)	5.1(5)
O2	0.263(2)	0.034(1)	0.577(1)	4.5(5)
N1	0.000(2)	0.287(1)	0.405(1)	2.1(4)
N2	0.400(2)	0.196(1)	0.567(1)	2.7(5)
C1	0.084(3)	0.364(1)	0.404(2)	2.9(6)

Table 10. (Continued)

Atom	x	y	z	B^a, Å^2
C2	-0.067(3)	0.456(2)	0.316(2)	4.5(8)
C3	0.303(4)	0.366(3)	0.474(3)	4.9(9)
C4	0.447(3)	0.280(1)	0.546(2)	2.8(6)
C5	0.670(3)	0.285(2)	0.606(2)	4.9(8)
C6	-0.235(3)	0.297(2)	0.332(2)	4.1(7)
C7	-0.263(4)	0.209(2)	0.374(2)	5.8(8)
C8	0.570(3)	0.123(2)	0.658(2)	3.4(7)
C9	0.501(3)	0.052(2)	0.689(2)	4.1(7)

[a]Isotropic thermal parameter, B, fitted to the expression, $\exp(-B\sin^2\theta/\lambda^2)$, while the anisotropic thermal parameters, β_{nm}, referred to in footnotes, b and c, were obtained by least-squares fitting to the expression: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

[b]Tabulated B is the isotropic value obtained prior to converting to anisotropic thermal motion. The refined anisotropic terms (x 10^4) are: β_{11} = 0.025(1), β_{22} = 0.0065(5), β_{33} = 0.083(6), β_{12} = -0.0061(6), β_{13} = 0.0118(8), β_{23} = 0.0007(4)

[c]Tabulated B is the isotropic value obtained prior to converting to anisotropic thermal motion. The refined anisotropic terms (x 10^4) are: β_{11} = 0.016(1), β_{22} = 0.0078(5), β_{33} = 0.0084(6), β_{12} = 0.0015(6), β_{13} = 0.0081(7), β_{23} = 0.0036(4)

Table 11. Observed and Calculated Structure Factors for $[Ni(H\cdot DIIMINE)]_2$

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
	L=	0		1	6	27	22	-4	-2	22	25	0	-10	15	13
				3	6	37	40	-3	-2	13	20	1	-10	35	37
2	-9	16	13	4	6	39	38	-2	-2	28	25	4	-10	15	16
-5	-5	32	34	-5	7	19	22	0	-2	11	10	-4	-9	22	21
-3	-2	11	13	-4	7	36	35	2	-2	59	56	-3	-9	16	17
2	0	61	56	-2	7	45	45	3	-2	35	34	-1	-9	19	18
3	0	61	63	-1	7	62	61	4	-2	21	19	0	-9	43	46
4	0	37	37	0	7	45	45	-3	-1	30	27	1	-9	19	20
5	0	13	15	2	7	34	35	1	-1	165	165	3	-9	18	19
-5	1	27	26	3	7	34	32	2	-1	50	48	4	-9	21	21
-4	1	47	50	5	7	17	17	3	-1	32	35	-4	-8	17	18
-3	1	35	35	-6	8	17	18	-2	0	58	60	-2	-8	27	25
-2	1	90	84	-5	8	15	16	1	0	59	54	-1	-8	71	56
1	1	68	75	-3	8	25	27	2	0	19	18	1	-8	26	32
2	1	69	74	-2	8	35	40	3	0	20	18	2	-8	28	27
3	1	77	80	-1	8	31	34	-6	1	12	8	3	-8	23	25
5	1	14	13	0	8	24	12	-5	1	12	13	5	-8	16	17
-5	2	37	39	1	8	41	42	-3	1	22	24	-6	-7	14	9
-3	2	45	45	2	8	33	36	-2	1	12	31	-5	-7	16	15
-2	2	86	82	4	8	15	17	0	1	18	21	-3	-7	41	40
-1	2	15	19	5	8	17	10	1	1	20	23	-2	-7	40	43
0	2	70	78	-4	9	14	16	3	1	16	15	0	-7	44	42
1	2	56	57	-3	9	17	15	-4	2	13	10	1	-7	60	59
2	2	44	47	0	9	43	42	0	2	59	55	2	-7	25	28
4	2	31	25	1	9	36	36	1	2	12	9	3	-7	16	12
5	2	27	27	3	9	27	27	2	2	21	25	4	-7	22	24
-4	3	68	62	-5	10	14	13	-4	3	19	21	5	-7	20	20
-3	3	30	29	-4	10	14	14	-2	3	25	20	-6	-6	19	17
-1	3	29	30	-1	10	32	30	2	3	14	12	-4	-6	45	46
0	3	52	53	0	10	19	21	-5	4	35	35	-3	-6	47	50
1	3	51	49	2	10	29	24	-4	4	13	12	-1	-6	56	54
3	3	75	76	3	10	27	25	-1	4	32	28	0	-6	88	88
4	3	46	48	-2	11	17	18	1	4	35	34	1	-6	44	42
-5	4	36	33	1	11	26	26	2	4	21	26	2	-6	20	18
-4	4	50	47	2	11	22	22	-4	5	15	16	4	-6	18	15
-3	4	13	14					-1	5	22	19	-6	-5	17	17
-2	4	41	41		L=	1		0	5	36	35	-5	-5	43	47
-1	4	82	82					1	5	22	20	-4	-5	35	36
0	4	40	38	0	-10	17	17	-3	6	27	22	-2	-5	32	28
1	4	28	27	2	-9	15	16	0	6	14	15	-1	-5	82	77
2	4	74	72	-2	-7	15	17	1	6	25	28	1	-5	38	39
3	4	57	59	-1	-7	16	17	0	7	14	10	2	-5	39	37
5	4	20	20	-2	-6	12	8	1	7	14	7	3	-5	27	26
-5	5	22	20	-1	-6	12	17					-7	-4	17	17
-3	5	39	45	1	-6	24	19		L=	2		-6	-4	24	25
-2	5	91	90	2	-6	18	15					-5	-4	17	18
-1	5	54	48	3	-6	15	14	1	-13	19	18	-4	-4	16	17
0	5	39	38	-2	-5	25	28	0	-12	17	19	-3	-4	68	68
1	5	77	77	-1	-5	30	30	1	-12	15	12	-2	-4	57	59
2	5	39	41	4	-5	14	16	-2	-11	23	22	0	-4	33	36
4	5	26	26	-2	-4	13	14	-1	-11	17	15	1	-4	91	77
-4	6	33	33	1	-4	39	39	1	-11	17	20	2	-4	27	29
-3	6	46	49	4	-4	12	15	2	-11	21	22	4	-4	27	27
-2	6	19	23	-3	-3	20	26	3	-11	15	13	5	-4	20	24
-1	6	78	77	-1	-3	38	28	-3	-10	29	25	-7	-3	14	12
0	6	61	68	4	-3	27	25	-2	-10	32	32	-6	-3	15	12

Table 11. (Continued

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-5	-3	14	16	1	2	55	52	-4	9	15	20	-2	3	11	10
-4	-3	50	50	2	2	64	60	-3	9	17	15	-1	3	31	30
-3	-3	48	52	4	2	26	30	0	9	25	26	0	3	19	18
-2	-3	14	15	5	2	25	23	1	9	21	22	1	3	12	12
-1	-3	87	85	-7	3	19	21	-1	10	21	22	-5	4	30	29
0	-3	52	57	-6	3	13	13	0	10	15	14	-1	4	25	21
1	-3	37	36	-4	3	25	25	2	10	19	19	0	4	19	18
3	-3	63	65	-3	3	40	39	-2	11	19	19	1	4	16	13
4	-3	67	71	-2	3	19	15	1	11	21	20	-6	5	16	17
-5	-2	32	31	-1	3	47	41	-3	12	15	14	-5	5	15	21
-4	-2	72	69	0	3	72	77	0	12	16	16	-5	6	18	19
-2	-2	85	83	1	3	47	45					-2	7	18	18
-1	-2	70	66	2	3	23	28		L=	3					
0	-2	54	56	3	3	63	65						L=	4	
2	-2	80	90	4	3	23	22	-1	-11	17	15				
3	-2	73	74	-5	4	60	62	-2	-10	18	16	-3	-10	19	20
5	-2	20	24	-4	4	36	35	-4	-9	17	22	-1	-10	15	19
6	-2	17	16	-2	4	44	43	-3	-9	17	12	1	-10	22	23
-6	-1	23	23	-1	4	89	82	-1	-9	15	8	-4	-9	23	21
-5	-1	28	30	0	4	70	65	-4	-8	13	13	-3	-9	20	18
-4	-1	17	19	1	4	28	28	1	-8	13	7	-2	-9	19	20
-3	-1	82	85	2	4	69	73	-3	-6	13	12	0	-9	37	39
-2	-1	53	57	3	4	35	35	1	-6	14	13	1	-9	16	13
0	-1	47	47	-6	5	19	19	-2	-5	38	32	-5	-8	18	16
1	-1	141	128	-5	5	30	30	0	-5	35	31	-4	-8	28	27
2	-1	61	64	-3	5	38	37	-4	-4	20	14	-2	-8	44	42
4	-1	46	46	-2	5	95	93	-3	-4	19	18	-1	-8	47	49
5	-1	15	16	-1	5	39	38	-1	-4	15	11	2	-8	17	20
-8	0	15	9	0	5	37	35	1	-4	28	27	-5	-7	27	27
-7	0	25	25	1	5	57	55	2	-4	14	20	-4	-7	15	16
-6	0	18	19	2	5	42	44	-5	-3	26	25	-3	-7	55	55
-4	0	65	57	4	5	16	17	-4	-3	39	39	-2	-7	56	60
-3	0	62	61	5	5	19	17	-1	-3	34	27	0	-7	40	38
-2	0	35	39	-7	6	15	10	0	-3	18	20	1	-7	35	46
0	0	135	154	-4	6	32	34	-5	-2	21	23	2	-7	16	18
1	0	45	42	-3	6	50	53	-4	-2	31	26	-6	-6	22	23
2	0	30	23	-2	6	17	24	1	-2	10	6	-5	-6	12	11
3	0	38	36	-1	6	34	33	2	-2	38	40	-4	-6	60	62
4	0	33	31	0	6	52	50	3	-2	15	9	-3	-6	37	36
-8	1	23	21	1	6	29	26	5	-2	12	9	-2	-6	20	20
-6	1	24	23	3	6	22	19	-1	-1	16	11	-1	-6	42	43
-5	1	33	33	4	6	25	26	0	-1	19	19	0	-6	60	58
-4	1	36	35	-5	7	21	18	1	-1	30	27	1	-6	27	30
-2	1	16	20	-4	7	23	21	2	-1	14	16	3	-6	25	24
-1	1	152	164	-2	7	46	48	3	-1	12	7	-6	-5	19	19
0	1	49	53	-1	7	49	53	-4	0	47	45	-5	-5	42	41
2	1	58	59	0	7	22	23	-2	0	12	16	-4	-5	38	38
3	1	38	36	2	7	26	28	-1	0	27	26	-3	-5	13	10
5	1	13	11	3	7	25	26	-6	1	11	6	-2	-5	16	11
6	1	21	17	-6	8	14	14	-2	1	17	18	-1	-5	78	74
-7	2	13	15	-5	8	17	15	-1	1	169	174	0	-5	65	66
-6	2	28	26	-3	8	33	19	0	1	20	21	1	-5	14	13
-5	2	36	32	-2	8	36	40	-5	2	10	8	2	-5	34	32
-3	2	35	33	0	8	15	18	-1	2	16	16	3	-5	14	11
-1	2	27	32	1	8	22	20	2	2	12	12	-6	-4	36	38
0	2	75	71	2	8	26	25	3	2	14	11	-5	-4	16	17

Table 11. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-2	-4	34	41	-1	2	27	32	-4	-3	40	36	0	-5	29	30
-1	-4	34	32	1	2	48	51	-2	-3	11	6	1	-5	17	13
0	-4	56	52	2	2	43	43	0	-3	37	34	2	-5	26	24
1	-4	54	54	-7	3	20	21	-6	-2	18	18	-7	-4	26	27
2	-4	32	32	-6	3	21	22	-4	-2	11	7	-6	-4	47	50
-7	-3	19	20	-4	3	28	34	-2	-2	30	24	-5	-4	40	39
-6	-3	18	19	-3	3	33	31	2	-2	15	13	-2	-4	76	73
-5	-3	13	10	-1	3	61	65	3	-2	22	22	-1	-4	37	33
-4	-3	43	44	0	3	49	47	-5	-1	20	21	1	-4	31	30
-3	-3	56	55	1	3	51	53	-2	-1	11	11	2	-4	18	14
-1	-3	65	61	3	3	23	23	2	-1	16	15	-7	-3	42	43
0	-3	90	83	-5	4	39	35	-3	0	11	14	-6	-3	18	23
1	-3	27	27	-4	4	22	15	3	0	15	13	-5	-3	18	16
3	-3	45	46	-2	4	19	14	-2	1	33	32	-4	-3	82	68
-7	-2	13	11	-1	4	57	56	-1	1	30	28	-3	-3	56	51
-5	-2	54	49	0	4	32	32	-4	2	14	15	-1	-3	47	46
-4	-2	83	79	2	4	44	44	-2	2	61	62	0	-3	61	59
-3	-2	11	17	-6	5	42	42	-1	2	16	15	1	-3	26	29
-2	-2	91	87	-5	5	30	28	-5	3	11	7	-8	-2	20	21
-1	-2	50	47	-3	5	33	40	-1	3	34	34	-7	-2	20	19
0	-2	36	31	-2	5	44	43	-6	5	18	25	-6	-2	35	33
1	-2	18	25	-1	5	18	18	1	6	14	12	-5	-2	82	84
2	-2	52	52	1	5	34	35					-4	-2	72	67
3	-2	54	55	2	5	27	30		L=	6		-2	-2	51	50
-6	-1	40	43	-6	6	19	22					-1	-2	75	71
-5	-1	53	52	-4	6	26	29	-3	-10	16	18	0	-2	16	16
-3	-1	30	33	-3	6	44	44	-5	-9	19	17	1	-2	13	9
-2	-1	50	50	-1	6	16	17	-4	-9	39	38	2	-2	36	33
-1	-1	31	34	0	6	36	39	-3	-9	44	42	-7	-1	17	19
0	-1	37	31	1	6	18	21	-2	-9	13	17	-6	-1	68	66
1	-1	38	38	-5	7	26	27	-1	-9	27	27	-5	-1	83	82
2	-1	26	25	-4	7	23	23	0	-9	32	34	-3	-1	90	87
-7	0	26	31	-2	7	25	32	-5	-8	49	50	-2	-1	73	67
-6	0	21	17	-1	7	27	28	-4	-8	46	42	-1	-1	29	29
-5	0	16	19	-5	8	15	15	-2	-8	37	38	0	-1	13	16
-4	0	98	90	-3	8	24	33	-1	-8	45	51	1	-1	25	23
-3	0	69	64	-2	8	21	27	0	-8	15	15	2	-1	33	34
-2	0	25	26	-3	9	16	18	-6	-7	27	27	-7	0	38	37
-1	0	29	30					-5	-7	43	40	-6	0	43	48
0	0	20	12		L=	5		-3	-7	63	63	-5	0	15	11
1	0	21	15					-2	-7	56	56	-4	0	98	91
3	0	32	32	-4	-9	13	17	1	-7	15	11	-3	0	68	67
-6	1	17	19	-3	-9	16	17	-7	-6	26	27	-2	0	25	23
-5	1	56	58	-6	-7	20	23	-6	-6	21	21	-1	0	19	16
-4	1	47	49	-1	-6	22	24	-5	-6	22	23	0	0	35	34
-2	1	60	57	0	-6	16	17	-4	-6	45	45	1	0	21	15
-1	1	135	131	-5	-5	12	10	-3	-6	40	41	-8	1	27	29
0	1	19	17	-4	-5	14	11	-1	-6	26	18	-7	1	30	34
1	1	18	26	-2	-5	51	42	0	-6	37	37	-6	1	14	15
2	1	29	26	-1	-5	35	33	1	-6	25	30	-5	1	93	93
3	1	30	28	-7	-4	14	11	-7	-5	16	17	-4	1	55	55
-7	2	20	22	-6	-4	13	14	-5	-5	55	53	-3	1	18	16
-6	2	42	45	-4	-4	13	12	-4	-5	28	28	-2	1	37	44
-5	2	33	33	-2	-4	22	14	-3	-5	13	10	-1	1	51	47
-3	2	34	31	-1	-4	23	18	-2	-5	33	30	2	1	21	18
-2	2	99	91	-5	-3	27	28	-1	-5	48	47	-7	2	21	22

Table 11. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-6	2	42	38	-1	-4	29	34	-1	-4	29	29	-2	3	13	16
-5	2	23	22	-4	-3	46	43	0	-4	16	19	-1	3	24	25
-3	2	31	37	-3	-3	28	27	1	-4	27	28	0	3	28	27
-2	2	95	103	-4	-2	28	28	-8	-3	29	30	-7	4	27	30
-1	2	24	28	-3	-2	15	13	-7	-3	46	49	-5	4	54	53
1	2	29	28	-4	-1	20	22	-6	-3	29	33	-4	4	53	53
2	2	22	24	-3	-1	31	23	-5	-3	22	21	-2	4	46	50
-7	3	27	24	-2	-1	24	26	-4	-3	24	31	-1	4	27	24
-6	3	29	25	-6	0	16	20	-3	-3	75	73	-6	5	46	49
-4	3	19	24	-4	0	44	41	-2	-3	32	25	-5	5	40	34
-3	3	23	27	-3	0	22	21	-1	-3	31	31	-3	5	28	27
-2	3	13	17	-7	1	20	21	0	-3	43	46	-2	5	22	22
-1	3	33	28	-3	2	13	16	1	-3	16	18	-6	6	22	21
0	3	40	39	-2	2	42	47	-8	-2	34	32	-4	6	17	16
1	3	28	26	-5	4	22	22	-7	-2	16	14	-3	6	24	23
-7	4	17	15	-4	4	30	34	-6	-2	34	35	-4	7	22	21
-5	4	31	27	-6	5	13	17	-5	-2	78	79				
-4	4	33	29	-5	5	28	32	-4	-2	70	64		L=	9	
-3	4	13	14					-3	-2	25	20				
-2	4	52	54		L=	8		-2	-2	61	63	-3	-10	17	12
-1	4	34	35					-1	-2	75	75	-3	-9	20	18
0	4	21	20	-5	-10	18	22	0	-2	19	21	-3	-7	17	19
-7	5	14	10	-3	-10	17	21	-7	-1	30	30	-7	-6	25	22
-6	5	51	56	-2	-10	24	28	-6	-1	53	55	-5	-6	15	12
-5	5	37	36	-6	-9	21	20	-5	-1	81	78	-5	-5	15	14
-3	5	30	31	-5	-9	16	10	-3	-1	85	86	-7	-4	18	18
-2	5	35	35	-4	-9	43	45	-2	-1	66	64	-8	-3	14	16
-6	6	34	36	-3	-9	20	20	0	-1	17	15	-5	-3	14	14
-4	6	33	34	-1	-9	27	33	1	-1	30	29	-4	-3	34	36
-3	6	40	35	-6	-8	21	16	-7	0	46	47	-4	-2	26	30
-2	6	16	16	-5	-8	53	53	-6	0	63	66	-2	-2	15	17
-1	6	16	17	-4	-8	44	44	-4	0	69	69	-5	-1	14	16
0	6	23	23	-1	-8	36	37	-3	0	49	46	-3	-1	15	17
-6	7	16	23	-7	-7	14	16	-2	0	14	13	-6	3	18	18
-5	7	18	18	-6	-7	51	51	-1	0	25	28	-4	3	23	19
-4	7	30	34	-5	-7	37	32	0	0	22	19	-1	3	17	18
-3	7	20	16	-3	-7	46	43	1	0	17	18	-5	4	31	32
-1	7	20	22	-2	-7	40	41	-8	1	25	25	-4	4	32	31
-3	8	20	27	-7	-6	17	19	-7	1	24	23	-6	5	18	22
-2	8	20	21	-6	-6	32	30	-5	1	52	60	-5	5	15	21
				-5	-6	13	21	-4	1	37	40				
	L=	7		-4	-6	54	57	-2	1	25	27		L=	10	
				-3	-6	42	42	-1	1	29	25				
-2	-10	15	12	-1	-6	29	27	-7	2	16	13	-6	-9	24	24
-3	-9	13	12	0	-6	24	23	-6	2	41	42	-4	-9	24	25
-2	-8	22	26	-8	-5	34	35	-5	2	32	35	-3	-9	15	15
-6	-7	13	9	-7	-5	20	21	-3	2	40	47	-6	-8	17	15
-3	-7	13	11	-6	-5	32	30	-2	2	56	57	-5	-8	48	49
-7	-6	27	23	-5	-5	64	67	-1	2	13	13	-4	-8	30	27
-5	-6	13	12	-4	-5	38	38	0	2	16	21	-2	-8	32	36
-3	-6	13	14	-2	-5	43	43	-8	3	18	17	-7	-7	26	24
-1	-6	21	24	-1	-5	46	48	-7	3	31	31	-6	-7	54	54
-5	-5	13	6	-6	-4	60	60	-6	3	27	31	-5	-7	42	44
-2	-5	17	22	-5	-4	42	38	-5	3	13	10	-3	-7	23	26
-3	-4	19	18	-3	-4	64	65	-4	3	48	46	-2	-7	35	35
-2	-4	16	15	-2	-4	69	72	-3	3	78	86	-8	-6	13	16

Table 11. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-7	-6	34	35	-8	3	16	16	-6	5	32	31
-6	-6	35	35	-7	3	30	25	-5	-1	27	23
-5	-6	17	16	-6	3	23	22	-3	-1	20	20
-4	-6	61	63	-4	3	44	47	-8	0	14	16
-3	-6	43	44	-3	3	64	70	-7	0	26	31
-1	-6	16	17	-7	4	19	19	-6	0	21	22
-7	-5	20	19	-5	4	36	36	-4	0	29	28
-6	-5	27	25	-4	4	44	46	-3	0	23	22
-5	-5	48	46	-6	5	18	22	-8	1	20	23
-4	-5	43	44					-7	1	21	27
-2	-5	38	39		L=	11		-6	1	18	19
-1	-5	28	31					-5	1	33	30
-8	-4	17	15	-4	-8	16	18	-4	1	22	17
-6	-4	54	52	-3	-7	16	17	-7	2	15	15
-5	-4	31	35	-7	-6	13	10	-6	2	31	30
-4	-4	16	15	-7	-4	20	20	-5	2	17	12
-3	-4	48	49	-5	-3	23	23	-7	3	24	23
-2	-4	40	41	-5	-2	28	30				
-1	-4	17	21	-2	-2	13	8		L=	13	
-7	-3	48	48								
-6	-3	23	22		L=	12		-6	-7	18	19
-5	-3	18	18					-7	-6	28	27
-4	-3	41	38	-7	-8	15	15	-6	-6	16	16
-3	-3	56	59	-6	-8	17	15	-6	-5	16	14
-2	-3	28	30	-5	-8	26	26	-8	-3	16	18
-1	-3	25	27	-7	-7	21	18	-8	0	14	11
-9	-2	24	22	-6	-7	38	37	-7	0	14	11
-7	-2	22	20	-5	-7	23	22				
-6	-2	37	36	-3	-7	18	17		L=	14	
-5	-2	42	33	-8	-6	15	13				
-4	-2	45	39	-7	-6	23	23	-6	-7	14	15
-2	-2	41	38	-6	-6	18	19	-7	-6	24	25
-1	-2	39	39	-3	-6	38	40	-6	-6	18	15
-9	-1	28	29	-7	-5	14	14	-8	-5	22	22
-7	-1	32	31	-5	-5	39	38	-5	-5	28	30
-6	-1	61	60	-4	-5	37	37	-8	-4	14	14
-5	-1	38	34	-8	-4	13	14	-7	-4	23	22
-3	-1	43	43	-7	-4	14	14	-6	-4	37	40
-2	-1	43	43	-6	-4	40	40	-5	-4	21	19
-8	0	21	24	-5	-4	27	28	-8	-3	24	24
-7	0	36	41	-4	-4	13	16	-7	-3	39	36
-6	0	33	37	-3	-4	35	35	-6	-3	17	20
-4	0	35	35	-2	-4	23	25	-8	-2	32	27
-3	0	33	31	-7	-3	55	52	-5	-2	17	17
-1	0	16	18	-6	-3	22	20	-8	-1	16	12
-8	1	26	27	-5	-3	16	14	-5	-1	22	20
-5	1	33	32	-4	-3	38	43	-7	0	19	23
-4	1	33	31	-3	-3	28	31	-6	0	14	16
-2	1	21	21	-9	-2	30	33	-7	1	14	13
-1	1	30	28	-8	-2	45	43				
-7	2	18	16	-7	-2	21	18				
-6	2	47	48	-5	-2	25	22				
-5	2	30	36	-4	-2	31	33				
-4	2	13	13	-9	-1	25	23				
-3	2	30	29	-8	-1	16	13				
-2	2	46	46	-7	-1	15	18				

Solution of the Structure of $[Cu(H\cdot DIIMINE)]_2$

A green crystal having measured[6] dimensions of 0.093(1) x 0.178(1) x 0.835(1) mm. was mounted on a glass fiber with the long dimension of the crystal tilted approximately 45° with respect to the glass fiber. This orientation was chosen because it corresponded to the extinction direction of the crystal. Precession photographs indicated a triclinic crystal, P1 or $P\bar{1}$. Space group $P\bar{1}$ was assumed and later confirmed by the successful refinement of the structure.

The crystal was transferred to an automated Picker four-circle diffractometer from which the unit cell parameters were obtained by a least-squares refinement of 27 reflections. The cell parameters obtained were: $a = 10.240(2)$Å, $b = 9.554(1)$Å, $c = 11.656$Å, $\alpha = 97.961(8)°$, $\beta = 72.669(5)°$, $\gamma = 104.80(1)°$, and $V = 1050.16$Å^3 (25°C, molybdenum radiation, $\lambda = 0.7107$Å).

With the triclinic cell defined above, control cards for the diffractometer were punched and data collection was begun with the detector mounted 16 cm. from the crystal. Sometime during the data collection, a Delaunay reduction of the above cell parameters was performed. The calculation confirmed the triclinic description of the unit cell and, in addition, indicated a conventional reduced cell having parameters very close to those calculated for $[Ni(H\cdot DIIMINE)]_2$. The primitive reduced cell parameters obtained were: $a' = 9.555$Å, $b' = 13.023$Å, $c' = 11.656$Å, $\alpha' = 131.361°$, $\beta' = 97.96°$, and $\gamma' = 94.41°$. The trans-

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[6]The dimensions of the crystal were measured using a toolmaker's microscope.

formation matrix is:

$$\begin{bmatrix} a' \\ b' \\ c' \end{bmatrix} = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 1 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

The calculated density of 1.56 g-cm^{-3} based on two formula units per unit cell, agreed exactly with the observed density of 1.56(1) g-cm^{-3} measured by the flotation method using a mixture of n-heptane and carbon tetrachloride.

Since the reduced cell parameters of $[Ni(H\cdot DIIMINE)]_2$ and $[Cu(H\cdot DIIMINE)]_2$ were very much alike, it was obvious that the two structures were nearly identical and that the lattices were closely isomorphous. Intensity measurements were continued until a complete data set of 2289 reflections was collected of which only 1388 were accepted as significantly above background ($\sigma(I)/I < 0.30$; $p = 0.02$). Two standard reflections of indices -1,3,2 and 3,2,1 were checked at intervals of 50 reflections and showed no significant variation during the data collection. The measured intensities were corrected both for background and Lorentz polarization effects. Absorption corrections were also made, utilizing the "Gaussian Quadrature Technique" to evaluate the absorption integral, A, given by equation (13), where V is the crys-

$$A = \frac{1}{V} \cdot \int_V \exp(-\mu\tau) \cdot dV \qquad (13)$$

tal volume, μ the linear absorption coefficient and, τ the effective thick-

ness of the crystal relative to the path of the x-ray. A routine in Stewart's XRAY-70 program (54) was used to accomplish this evaluation. The numerical summation was accomplished over a 10 x 10 x 10 grid of points within the crystal volume. The measured intensities were corrected by the formula given in equation (14), where A*, the absorption

$$I(\text{corrected}) = A^* \cdot I(\text{measured}) \qquad (14)$$

correction, is the reciprocal of the absorption integral. The value of A* varied from a maximum of 1.725 for the 0,-8,1 reflection to a minimum of 1.197 for the 4,0,1 reflection. The Miller indices of the bounding planes of the crystal were: (001), (00$\bar{1}$), (1$\bar{1}$1), ($\bar{1}\bar{1}$1), (111) and ($\bar{1}\bar{1}\bar{1}$). The calculated linear absorption coefficient, μ, was 21.2 cm^{-1}.

In order to compare the final positional and thermal parameters of the $[Cu(H\cdot DIIMINE)]_2$ structure to those of the $[Ni(H\cdot DIIMINE)]_2$ structure, it was necessary to transform the indices (i.e. redefine the cell) so that the basis vectors of the $[Cu(H\cdot DIIMINE)]_2$ cell were nearly the same as those of the closely isomorphous $[Ni(H\cdot DIIMINE)]_2$ cell. The transformation matrix used was:

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix}_{Ni} = \begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 1 & 0 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix}_{Cu}$$

The subscripts, Ni and Cu, refer to the indices based upon the cells of the $[Ni(H\cdot DIIMINE)]_2$ and $[Cu(H\cdot DIIMINE)]_2$ crystals respectively. Once

the indices were transformed, the refined coordinates and thermal parameters of the atoms from the $[Ni(H\cdot DIIMINE)]_2$ structure could be used as starting values in the refinement of the coordinates and thermal parameters of the $[Cu(H\cdot DIIMINE)]_2$ structure. When this was done, the full-matrix least-squares refinement of the scale factor, coordinates and thermal parameters converged rapidly to their proper values. A weighting scheme was applied, and anisotropic thermal parameters were refined for the copper atoms. The final residuals, R_1 and R_2, were 0.0796 and 0.0657, respectively. The positional and thermal parameters from the last cycle of least-squares refinement are presented in Table 12. The observed and calculated structure factors for all 1272 unique nonzero reflections are given in Table 13.

Molecular Weight Studies

Table 14 contains a summary of the data obtained by osmometry on the molecular weights of the metal diimine complexes in various solvents. All the measurements were taken with a Model 301A Mechrolab Vapor Pressure Osmometer at a temperature of 37°C. Calibration curves were obtained for all solvents (technical grade) using either benzil or sodium chloride as the calibrant. When sample readings were taken over a period longer than one day's time, a new calibration curve was determined before that day's measurements were recorded. In addition, whenever the solvent in the chamber was changed or renewed, the instrument was allowed to equilibrate for at least twelve hours prior to the collection of any data. At the end of that time the "drift" of the needle due to a lack of equilibrium in the system was well within the tolerances specified by

Table 12. Final Positional and Thermal Parameters for $[Cu(H\cdot DIIMINE)]_2$

Atom	x	y	z	B^a, $Å^2$
UNIT 1				
Cu	0.1439(5)	0.1611(2)	-0.0012(3)	3.70(8)[b]
O1	0.079(2)	-0.013(1)	-0.076(1)	5.8(4)
O2	0.092(2)	0.159(1)	0.097(1)	4.5(3)
N1	0.196(2)	0.158(1)	-0.095(1)	3.6(4)
N2	0.200(2)	0.331(1)	0.070(1)	3.3(3)
C1	0.245(2)	0.255(1)	-0.099(1)	3.1(4)
C2	0.267(3)	0.234(2)	-0.196(2)	7.2(7)
C3	0.290(4)	0.371(2)	-0.021(2)	5.3(6)
C4	0.270(2)	0.407(1)	0.057(1)	3.3(4)
C5	0.349(3)	0.543(1)	0.148(2)	5.0(6)
C6	0.146(3)	0.038(1)	-0.185(1)	4.7(5)
C7	0.131(3)	-0.054(2)	-0.142(2)	7.2(8)
C8	0.202(3)	0.376(1)	0.169(2)	5.0(6)
C9	0.041(3)	0.276(1)	0.122(2)	5.1(6)
UNIT 2				
Cu	0.1336(5)	0.1670(3)	0.4982(3)	3.70(8)[c]
O1	-0.141(2)	0.121(1)	0.421(1)	5.6(4)
O2	0.274(2)	0.034(1)	0.585(1)	5.9(4)
N1	-0.005(2)	0.295(1)	0.409(1)	3.5(4)
N2	0.404(2)	0.207(1)	0.571(1)	2.9(3)
C1	0.078(2)	0.367(1)	0.404(1)	3.5(4)

Table 12. (Continued)

Atom	x	y	z	B^a, $Å^2$
C2	-0.076(3)	0.461(1)	0.314(2)	5.4(6)
C3	0.288(3)	0.367(2)	0.469(2)	3.5(5)
C4	0.435(3)	0.287(1)	0.546(1)	4.0(5)
C5	0.668(3)	0.301(1)	0.604(1)	5.5(6)
C6	-0.240(3)	0.298(1)	0.330(1)	4.2(5)
C7	-0.285(4)	0.208(2)	0.363(2)	8.0(8)
C8	0.576(3)	0.127(1)	0.658(2)	5.1(6)

[a]Isotropic thermal parameter, B, fitted to the expression, $\exp(-B\sin^2\theta/\lambda^2)$, while the anisotropic thermal parameters, β_{nm}, referred to in footnotes, b and c, were obtained by least-squares fitting to the expression: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

[b]Tabulated B is the isotropic value obtained prior to converting to anisotropic thermal motion. The refined anisotropic terms ($\times 10^4$) are: $\beta_{11} = 0.026(1)$, $\beta_{22} = 0.0068(3)$, $\beta_{33} = 0.0096(5)$, $\beta_{12} = 0.0003(4)$, $\beta_{13} = 0.0127(6)$, $\beta_{23} = 0.0009(3)$

[c]Tabulated B is the isotropic value obtained prior to converting to anisotropic thermal motion. The refined anisotropic terms ($\times 10^4$) are: $\beta_{11} = 0.0177(9)$, $\beta_{22} = 0.0091(3)$, $\beta_{33} = 0.0112(5)$, $\beta_{12} = 0.0030(4)$, $\beta_{13} = 0.0101(6)$, $\beta_{23} = 0.0050(3)$

Table 13. Observed and Calculated Structure Factors for $[Cu(H\cdot DIIMINE)]_2$

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
	K= 0			-3	10	27	28	7	-12	16	20	1	-4	28	34
				-3	8	50	46	7	-13	14	14	1	-5	5	8
8	-8	9	11	-3	7	23	26	7	-14	12	11	1	-8	11	11
8	-10	21	22	-3	6	68	66	6	-2	26	27	0	8	14	14
8	-11	11	10	-3	4	69	67	6	-5	9	8	0	6	17	15
8	-12	15	17	-3	3	10	8	6	-6	66	68	0	4	18	15
8	-13	12	13	-3	2	65	65	6	-8	58	55	0	2	44	46
8	-14	15	15	-3	0	60	62	6	-11	7	7	0	1	15	15
7	-10	33	37	-3	-2	41	38	6	-12	28	30	0	-1	9	11
7	-12	24	26	-3	-4	30	32	6	-14	12	9	0	-2	42	43
6	-1	7	6	-3	-5	12	11	5	0	12	11	0	-3	14	16
6	-8	58	58	-4	12	26	26	5	-2	25	26	0	-4	34	32
6	-10	26	31	-4	10	33	32	5	-3	7	5	0	-6	18	15
6	-12	19	19	-4	8	66	63	5	-4	50	50	1	9	9	14
5	-2	15	14	-4	7	38	34	5	-5	11	16	1	8	29	26
5	-6	23	23	-4	4	101	96	5	-6	82	80	1	6	50	45
5	-7	12	10	-4	3	46	43	5	-7	13	11	1	-2	125	125
5	-8	11	15	-4	-1	6	4	5	-8	75	73	1	-3	25	22
5	-10	13	19	-4	-2	34	32	5	-9	13	13	1	-4	37	38
4	0	39	43	-5	11	6	7	5	-10	32	32	1	-6	28	26
4	-1	5	9	-5	9	15	14	5	-12	23	20	2	10	19	18
4	-2	63	60	-5	4	24	26	4	2	8	7	2	8	30	32
4	-5	7	7	-5	0	16	16	4	0	15	15	2	6	43	52
4	-6	97	96	-5	-1	7	6	4	-2	23	23	2	5	35	39
3	1	20	19	-6	14	16	15	4	-3	6	7	2	4	61	64
3	-5	19	19	-6	7	22	22	4	-4	15	17	2	3	20	20
3	-9	6	9	-6	6	40	42	4	-6	14	15	2	2	11	20
3	-9	6	9	-6	5	11	12	4	-7	26	28	2	1	31	31
2	1	15	10	-6	4	16	16	3	4	28	27	2	0	96	95
2	-1	57	57	-6	3	8	2	3	2	40	40	2	-1	50	50
2	-3	7	10	-6	2	14	16	3	1	12	11	2	-2	67	71
2	-8	9	11	-7	14	21	25	3	0	81	79	2	-3	9	12
1	5	6	4	-7	13	8	7	3	-1	32	30	2	-4	28	27
1	2	44	46	-7	8	42	45	3	-2	91	89	2	-5	15	14
0	4	20	19	-7	7	9	8	3	-4	33	33	2	-6	32	29
0	-6	37	33	-7	6	38	39	3	-6	88	89	3	11	8	7
0	-7	10	5	-7	5	11	8	3	-7	25	24	3	10	11	11
0	-8	24	20	-7	4	32	36	3	-8	79	78	3	7	6	3
-1	9	7	6	-8	6	16	19	3	-9	10	9	3	6	11	11
-1	8	27	27					3	-10	38	38	3	2	14	8
-1	6	20	20		K= 1			3	-11	8	8	3	1	20	25
-1	5	8	8					2	6	20	18	3	0	29	27
-1	4	32	35	9	-11	8	5	2	0	78	78	3	-1	25	27
-1	3	28	32	9	-12	21	20	2	-2	51	58	3	-2	6	2
-1	1	6	7	8	-7	6	6	2	-4	49	52	3	-3	9	3
-1	-1	64	60	8	-8	10	5	2	-5	12	14	4	12	18	16
-1	-4	21	19	8	-9	10	4	2	-6	69	70	4	10	30	27
-1	-6	23	16	8	-11	9	10	2	-7	28	30	4	9	8	14
-1	-7	7	4	8	-12	7	5	2	-8	63	63	4	8	35	38
-2	10	6	5	8	-14	8	7	2	-10	37	39	4	6	51	53
-2	7	5	4	7	-4	9	12	1	5	6	4	4	5	9	9
-2	6	22	22	7	-5	9	6	1	4	15	25	4	4	47	47
-2	4	23	26	7	-6	18	22	1	2	4	6	4	3	10	7
-2	2	32	40	7	-8	33	32	1	1	18	18	4	2	38	38
-2	0	55	50	7	-10	34	33	1	0	67	74	4	1	11	12
-2	-2	24	15	7	-11	11	11	1	-3	10	8	4	0	48	53

Table 13. (Continued)

H	L	FO	FC
-4	-2	44	44
-4	-3	5	5
-5	12	31	27
-5	10	32	34
-5	9	10	7
-5	8	59	62
-5	7	11	13
-5	6	95	93
-5	4	57	61
-5	2	37	41
-5	1	12	11
-5	0	30	29
-6	12	19	20
-6	10	18	15
-6	9	9	8
-6	8	20	23
-6	7	11	12
-6	6	16	20
-6	3	15	9
-6	2	25	23
-6	1	9	8
-7	12	16	22
-7	10	10	12
-7	8	18	18
-7	7	24	21
-7	6	24	29
-7	5	14	13
-7	4	6	7
-7	3	6	4
-8	12	18	20
-8	10	23	22
-8	8	25	27
-8	7	10	5
-8	6	28	33

K= 2

H	L	FO	FC
9	-11	8	7
9	-12	32	34
8	-7	6	2
8	-8	33	31
8	-9	6	3
8	-10	45	45
8	-11	7	4
8	-12	39	39
8	-14	27	24
7	-4	11	9
7	-6	18	14
7	-7	5	7
7	-8	10	8
7	-9	7	6
7	-10	14	13
7	-13	9	9
7	-14	7	5
6	-3	6	11
6	-4	11	10
6	-5	12	13
6	-6	40	37
6	-7	11	8
6	-8	42	40
6	-10	38	36
6	-12	11	10
5	0	27	27
5	-2	33	32
5	-3	16	19
5	-4	57	54
5	-6	89	89
5	-8	82	82
5	-10	43	39
5	-11	19	23
5	-12	21	18
4	2	23	28
4	0	29	24
4	-1	23	25
4	-2	73	66
4	-3	32	28
4	-4	85	81
4	-5	8	7
4	-6	76	74
4	-7	30	27
4	-8	68	63
4	-9	23	27
4	-10	37	35
4	-12	25	27
3	0	10	14
3	-1	15	16
3	-2	10	14
3	-4	18	22
3	-7	15	14
3	-9	17	15
2	4	40	41
2	3	7	6
2	2	65	62
2	1	18	21
2	0	50	53
2	-1	29	23
2	-2	71	80
2	-4	66	83
2	-5	27	22
2	-6	54	54
2	-8	59	63
2	-10	35	35
1	6	26	26
1	5	6	4
1	4	47	48
1	2	56	56
1	1	10	12
1	0	57	59
1	-2	68	66
1	-4	49	48
1	-5	6	8
1	-6	71	73
1	-8	74	74
0	8	13	14
0	6	7	6
0	4	19	12
0	3	16	10
0	2	72	71
0	1	58	57
0	0	69	61
0	-1	12	10
0	-2	56	60
0	-4	34	33
0	-6	18	19
0	-8	17	20
-1	9	8	11
-1	8	16	12
-1	6	21	24
-1	5	6	4
-1	4	8	23
-1	2	11	22
-1	0	13	17
-1	-1	14	9
-1	-4	19	23
-1	-5	6	5
-1	-6	14	11
-2	10	39	39
-2	9	13	20
-2	8	57	57
-2	7	34	39
-2	6	95	99
-2	5	53	57
-2	4	96	91
-2	3	12	6
-2	0	94	87
-2	-1	54	54
-2	-2	80	86
-2	-3	28	29
-2	-4	52	53
-2	-6	32	31
-3	10	27	28
-3	8	49	54
-3	7	16	15
-3	6	36	41
-3	4	34	30
-3	2	40	37
-3	0	55	54
-3	-1	30	31
-3	-2	78	79
-3	-4	52	52
-3	-5	18	18
-4	11	6	9
-4	10	8	8
-4	9	7	8
-4	6	4	4
-4	5	14	14
-4	4	6	7
-4	2	12	17
-4	1	17	17
-4	-1	18	16
-5	12	14	11
-5	11	8	9
-5	9	14	14
-5	8	31	34
-5	7	7	12
-5	6	22	23
-5	5	6	5
-5	4	31	32
-5	3	5	6
-5	2	35	34
-5	1	7	6
-5	0	37	39
-5	-1	6	9
-6	12	28	27
-6	10	45	48
-6	9	11	9
-6	8	47	48
-6	6	43	45
-6	4	45	44
-6	2	26	25
-7	12	17	17
-7	10	21	21
-7	9	7	6
-7	8	17	18
-7	6	25	25
-7	5	10	11
-7	4	22	22
-8	12	7	6
-8	11	6	7
-8	8	8	5
-8	7	11	12

K= 3

H	L	FO	FC
8	-9	17	19
8	-10	18	19
8	-12	12	10
8	-13	13	13
8	-14	22	20
7	-4	19	21
7	-6	42	41
7	-7	8	6
7	-8	48	48
7	-10	47	46
7	-12	50	49
7	-14	34	33
6	-2	13	10
6	-4	18	18
6	-6	17	21
6	-7	14	11
6	-8	21	24
6	-10	21	18
6	-11	10	9
6	-12	20	20

Table 13. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
6	-13	8	5	1	-2	90	90	-4	2	32	33	6	-11	6	6
6	-14	14	16	1	-3	32	24	-4	1	25	27	6	-12	38	40
5	0	10	10	1	-4	64	64	-4	0	75	70	6	-13	8	8
5	-2	15	14	1	-6	51	49	-4	-1	24	22	6	-14	34	35
5	-3	22	22	1	-7	6	4	-4	-2	67	66	5	-2	16	18
5	-4	17	11	1	-8	31	30	-5	11	8	7	5	-4	13	17
5	-5	27	27	0	6	39	39	-5	9	12	12	5	-6	36	36
5	-6	26	23	0	4	47	47	-5	8	13	8	5	-8	39	36
5	-7	5	8	0	3	17	20	-5	7	8	6	5	-9	9	6
5	-8	28	28	0	2	71	75	-5	6	8	12	5	-10	26	30
5	-9	14	12	0	1	5	9	-5	5	15	15	5	-11	8	3
5	-10	24	21	0	0	53	55	-5	4	11	11	5	-12	23	25
5	-11	14	14	0	-2	56	59	-5	3	10	13	5	-13	7	6
5	-12	11	9	0	-3	17	22	-5	2	25	20	4	1	6	2
5	-13	6	6	0	-4	90	88	-5	1	10	6	4	0	11	12
4	2	24	25	0	-5	37	35	-5	0	9	8	4	-2	19	18
4	0	46	47	0	-6	63	62	-6	11	7	8	4	-3	12	14
4	-1	5	3	0	-8	42	43	-6	10	20	18	4	-5	11	12
4	-2	54	50	-1	9	10	11	-6	9	20	23	4	-9	7	8
4	-3	40	38	-1	8	21	21	-6	8	28	29	4	-10	18	20
4	-4	50	51	-1	6	31	26	-6	7	8	8	4	-12	12	14
4	-5	37	35	-1	5	36	36	-6	6	26	26	3	2	32	34
4	-5	37	35	-1	4	60	65	-6	4	21	23	3	0	60	61
4	-6	94	84	-1	3	33	35	-6	3	6	6	3	-2	74	76
4	-7	40	35	-1	2	50	45	-6	2	12	13	3	-3	28	24
4	-8	33	37	-1	1	8	3	-7	12	24	24	3	-4	8	4
4	-9	29	31	-1	0	36	36	-7	10	30	27	3	-6	9	12
4	-10	40	38	-1	-1	13	12	-7	8	32	35	3	-7	24	22
4	-12	34	36	-1	-2	41	39	-7	6	28	28	3	-8	61	62
3	3	8	12	-1	-4	27	30	-7	4	19	22	3	-10	47	47
3	2	57	60	-1	-5	7	7	-8	10	18	15	2	4	39	40
3	1	11	6	-1	-6	24	26	-8	8	20	20	2	3	7	9
3	0	77	77	-2	10	10	9	-8	7	6	7	2	2	68	72
3	-1	27	30	-2	8	15	15					2	1	17	20
3	-2	56	56	-2	7	11	10		K= 4			2	0	76	75
3	-3	12	12	-2	6	8	10					2	-1	14	14
3	-4	56	57	-2	5	7	10	8	-8	8	6	2	-2	58	59
3	-5	12	10	-2	4	8	16	8	-10	11	12	2	-4	32	38
3	-6	54	54	-2	2	19	17	8	-12	9	12	2	-5	23	16
3	-7	31	30	-2	1	26	21	8	-13	5	9	2	-6	78	77
3	-8	72	70	-3	11	6	6	8	-14	12	11	2	-7	11	12
3	-10	50	52	-3	10	56	61	7	-5	9	11	2	-8	67	69
2	2	19	22	-3	8	79	82	7	-6	32	33	2	-10	35	36
2	-1	8	5	-3	6	29	28	7	-8	21	22	1	6	7	8
2	-2	16	18	-3	5	6	11	7	-9	13	9	1	5	7	6
2	-5	9	9	-3	4	36	36	7	-11	17	15	1	4	10	9
2	-6	7	5	-3	2	41	41	7	-12	19	18	1	3	8	8
2	-7	11	10	-3	0	36	38	7	-13	8	9	1	2	24	20
2	-8	29	32	-3	-2	63	64	7	-14	24	23	1	1	28	29
2	-10	22	21	-3	-4	38	37	6	-3	10	9	1	0	25	22
1	6	26	26	-4	10	40	42	6	-4	38	37	1	-3	15	9
1	4	51	50	-4	9	17	17	6	-5	13	14	1	-4	29	27
1	3	15	16	-4	8	51	46	6	-6	50	52	1	-5	20	21
1	2	52	49	-4	7	11	17	6	-8	59	55	1	-6	31	27
1	0	55	53	-4	6	27	27	6	-9	6	6	1	-7	21	25
1	-1	34	25	-4	4	33	35	6	-10	52	51	1	-8	27	30

Table 13. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
0	6	20	19	-4	1	13	11	5	-11	6	11	-1	2	43	41
0	5	6	5	-4	0	48	42	5	-12	33	35	-1	1	29	25
0	4	35	34	-4	-1	10	5	5	-13	8	8	-1	0	51	46
0	3	23	22	-4	-2	21	21	4	0	23	22	-1	-1	8	8
0	2	74	71	-5	10	31	27	4	-1	9	8	-1	-2	37	35
0	1	11	10	-5	9	26	30	4	-2	31	31	-1	-3	7	4
0	0	43	46	-5	8	55	50	4	-3	6	3	-1	-4	15	16
0	-1	6	6	-5	7	22	24	4	-4	35	36	-1	-6	16	15
0	-2	38	43	-5	6	37	34	4	-6	27	33	-2	8	20	18
0	-4	54	51	-5	4	47	44	4	-7	4	2	-2	7	10	11
0	-6	28	32	-5	3	35	36	4	-8	37	41	-2	6	34	34
0	-8	15	17	-5	2	62	62	4	-9	9	4	-2	4	47	48
-1	8	26	23	-5	1	33	33	4	-10	38	38	-2	2	99	99
-1	7	8	11	-5	0	34	34	4	-11	7	3	-2	1	8	6
-1	6	34	34	-6	11	9	8	4	-12	30	28	-2	0	97	95
-1	5	9	13	-6	9	9	12	3	0	8	10	-2	-1	5	2
-1	4	53	55	-6	8	13	11	3	-4	7	5	-2	-2	40	41
-1	3	26	26	-6	6	18	19	2	4	24	25	-2	-4	34	32
-1	2	89	83	-6	5	17	15	2	2	40	43	-2	-5	6	6
-1	1	31	31	-6	4	15	12	2	0	49	49	-2	-6	25	24
-1	0	86	89	-6	3	10	11	2	-1	27	30	-3	9	7	4
-1	-1	42	42	-6	2	7	10	2	-2	38	38	-3	8	29	28
-1	-2	98	86	-7	10	15	16	2	-3	41	31	-3	7	8	14
-1	-3	29	28	-7	9	10	11	2	-4	13	12	-3	6	34	30
-1	-4	55	54	-7	8	25	25	2	-5	46	36	-3	4	34	40
-1	-6	30	31	-7	7	9	10	2	-6	39	36	-3	3	9	9
-2	8	42	44	-7	6	14	16	2	-7	14	15	-3	2	42	42
-2	7	9	10	-7	4	8	10	2	-8	45	46	-3	1	8	5
-2	6	50	51					2	-10	36	38	-3	0	45	49
-2	5	12	7		K= 5			1	5	6	4	-3	-1	10	10
-2	4	23	20					1	4	33	33	-3	-2	29	28
-2	2	51	50	8	-10	9	11	1	2	55	53	-3	-3	10	10
-2	0	46	44	8	-14	22	21	1	1	21	23	-3	-4	14	14
-2	-1	7	9	7	-6	13	13	1	0	74	75	-4	7	8	7
-2	-2	28	29	7	-8	15	15	1	-1	34	31	-4	5	16	15
-2	-3	14	18	7	-9	6	5	1	-2	89	83	-4	2	6	8
-2	-4	31	30	7	-10	14	13	1	-3	14	13	-4	1	17	19
-2	-5	7	8	7	-12	9	11	1	-4	80	77	-4	0	7	11
-2	-6	17	17	7	-14	15	16	1	-5	34	35	-4	-1	14	16
-3	9	10	9	6	-4	22	21	1	-6	47	48	-5	10	14	14
-3	7	10	6	6	-6	11	8	1	-8	44	46	-5	9	17	19
-3	6	14	18	6	-7	12	14	0	6	8	7	-5	8	41	36
-3	4	5	3	6	-8	34	31	0	4	7	7	-5	7	29	31
-3	3	9	14	6	-10	27	25	0	2	33	32	-5	6	40	40
-3	1	11	7	6	-11	20	22	0	1	31	31	-5	5	6	8
-3	0	14	12	6	-13	11	14	0	0	37	35	-5	4	30	31
-3	-1	8	11	6	-14	13	13	0	-2	45	43	-5	3	10	7
-3	-2	11	10	5	-2	45	45	0	-3	35	32	-5	2	27	23
-3	-4	8	8	5	-3	7	6	0	-4	65	64	-5	0	15	16
-4	10	39	38	5	-4	40	40	0	-5	11	13	-6	10	19	19
-4	9	32	33	5	-5	9	8	0	-6	26	24	-6	9	15	18
-4	8	55	53	5	-6	55	55	0	-8	13	13	-6	8	47	48
-4	7	34	36	5	-7	7	6	-1	7	7	8	-6	7	13	12
-4	6	38	37	5	-8	69	71	-1	6	11	14	-6	6	56	60
-4	4	25	24	5	-9	10	6	-1	4	21	23	-6	5	20	23
-4	2	38	40	5	-10	44	42	-1	3	10	10	-6	4	46	44

Table 13. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
-6	3	11	15	2	-4	16	14	-3	-3	6	1	3	-10	24	24
-6	2	16	20	2	-5	7	4	-3	-4	27	26	3	-11	11	10
-7	9	10	9	2	-6	7	5	-4	8	19	19	2	2	27	27
-7	8	16	14	2	-10	6	4	-4	6	34	33	2	0	34	36
-7	6	15	16	1	4	23	22	-4	4	28	30	2	-1	9	9
				1	3	6	8	-4	2	35	37	2	-2	38	41
	K=	6		1	2	31	28	-4	0	36	36	2	-4	57	56
				1	1	25	27	-4	-2	17	20	2	-6	51	50
8	-10	15	17	1	0	26	24	-5	8	6	10	2	-8	39	38
8	-12	14	15	1	-1	19	23	-5	5	10	11	2	-9	8	11
7	-6	29	31	1	-2	57	57	-5	4	11	13	2	-10	35	37
7	-7	21	17	1	-4	42	43	-5	3	21	24	1	2	7	7
7	-8	17	23	1	-5	22	23	-5	2	14	13	1	1	9	7
7	-9	25	20	1	-6	29	24	-5	1	7	9	1	-1	20	18
7	-10	26	27	1	-7	18	19	-5	0	6	7	1	-2	9	10
7	-11	11	10	1	-8	30	31	-6	8	18	19	1	-3	9	8
7	-12	17	19	0	6	23	20	-6	7	12	10	1	-4	10	12
7	-13	21	20	0	4	34	32	-6	6	28	28	1	-5	6	5
7	-14	25	25	0	2	49	48	-6	5	11	13	1	-8	8	4
6	-4	17	19	0	1	11	12	-6	4	14	17	1	-9	6	6
6	-6	16	15	0	0	74	75					0	2	24	24
6	-8	28	25	0	-2	89	93		K=	7		0	1	14	14
6	-10	30	28	0	-4	59	55					0	0	44	41
6	-12	7	9	0	-5	16	17	7	-8	20	23	0	-1	10	11
6	-13	12	9	0	-6	37	36	7	-10	23	24	0	-2	46	46
6	-14	12	12	0	-8	25	24	7	-12	21	18	0	-4	42	38
5	-2	9	6	-1	6	11	10	6	-5	23	20	0	-5	8	9
5	-3	10	11	-1	4	15	13	6	-6	23	25	0	-6	14	13
5	-4	15	13	-1	2	37	36	6	-7	14	13	0	-8	8	6
5	-6	25	25	-1	0	82	82	6	-8	48	47	-1	6	21	21
5	-7	13	9	-1	-1	28	27	6	-10	50	49	-1	4	29	27
5	-8	25	29	-1	-2	47	45	6	-11	10	11	-1	2	50	53
5	-9	10	5	-1	-3	8	13	6	-12	31	32	-1	1	6	3
5	-10	16	18	-1	-4	27	31	6	-13	17	18	-1	0	62	59
5	-11	11	13	-1	-6	22	23	5	-4	24	21	-1	-2	63	60
5	-13	8	9	-2	8	11	11	5	-6	37	36	-1	-4	38	45
4	0	37	36	-2	7	12	12	5	-7	6	5	-1	-6	12	12
4	-2	46	45	-2	6	17	17	5	-8	34	29	-2	6	11	11
4	-4	59	61	-2	4	11	10	5	-9	6	4	-2	4	24	30
4	-5	7	9	-2	2	13	16	5	-10	38	36	-2	3	25	27
4	-6	46	50	-2	1	8	8	5	-12	16	15	-2	2	49	51
4	-8	56	61	-2	0	18	20	5	-13	9	8	-2	1	9	9
4	-10	58	57	-2	-1	18	17	4	-4	22	20	-2	0	50	47
4	-11	7	8	-2	-2	19	22	4	-5	7	3	-2	-1	11	6
4	-12	16	11	-2	-3	9	12	4	-6	11	16	-2	-2	25	28
3	2	20	18	-2	-4	10	5	4	-8	12	17	-2	-4	18	21
3	0	35	33	-3	8	23	22	4	-10	8	8	-3	7	10	10
3	-2	47	48	-3	6	39	36	3	0	33	33	-3	6	13	12
3	-3	9	6	-3	5	6	3	3	-2	44	44	-3	5	12	11
3	-4	35	40	-3	4	45	48	3	-3	6	2	-3	4	7	5
3	-6	36	40	-3	3	8	6	3	-4	57	56	-3	3	8	6
3	-7	11	11	-3	2	54	54	3	-5	10	7	-3	-2	10	9
3	-8	42	41	-3	1	26	25	3	-6	61	62	-3	-3	7	12
3	-10	40	40	-3	0	48	51	3	-7	13	12	-4	8	21	22
2	1	12	12	-3	-1	14	14	3	-8	50	49	-4	6	30	31
2	-1	11	11	-3	-2	41	39	3	-9	15	18	-4	4	22	23

Table 13. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
-4	3	7	6	1	1	9	10	-5	4	15	16	-1	-3	10	8
-4	2	24	25	1	0	38	40					-1	-4	14	12
-4	0	36	35	1	-2	46	49		K= 9			-2	0	12	13
-5	8	15	15	1	-3	7	4					-2	-1	16	16
-5	6	22	21	1	-4	45	45	6	-8	14	16	-2	-2	8	11
-5	4	26	26	1	-6	47	51	6	-10	18	17	-2	-3	10	10
-5	2	20	20	1	-7	6	9	5	-6	16	14	-3	4	17	18
-6	6	21	23	1	-8	39	39	5	-8	15	11	-3	2	20	17
-6	5	12	10	1	-9	8	7	5	-10	13	11	-3	1	7	6
				0	4	9	7	4	-3	17	16	-3	0	16	16
	K= 8			0	2	15	14	4	-4	22	23	-4	4	16	16
				0	0	22	13	4	-5	14	13	-4	2	15	16
7	-10	7	9	0	-1	10	9	4	-6	39	39				
6	-6	12	14	0	-4	13	13	4	-8	45	43		K=10		
6	-8	23	20	0	-5	9	6	4	-9	10	7				
6	-10	22	18	0	-6	17	16	4	-10	26	27	4	-6	12	10
6	-12	18	16	0	-8	7	7	4	-11	8	3	4	-8	13	11
5	-4	16	16	-1	4	7	5	3	-2	18	19	3	-3	9	9
5	-6	48	47	-1	2	14	13	3	-3	18	13	3	-4	18	19
5	-8	52	53	-1	1	8	9	3	-4	21	20	3	-5	13	10
5	-10	48	48	-1	0	31	32	3	-5	14	13	3	-6	19	20
5	-12	24	24	-1	-1	8	9	3	-6	44	42	3	-7	7	5
4	-2	16	17	-1	-2	31	31	3	-7	7	8	3	-8	22	24
4	-3	13	13	-1	-3	12	12	3	-8	19	19	3	-9	12	7
4	-4	30	30	-1	-4	10	14	3	-9	19	15	2	-2	28	28
4	-6	41	38	-1	-5	10	8	3	-10	14	16	2	-3	19	16
4	-8	41	38	-1	-6	6	5	2	-3	8	5	2	-4	9	8
4	-10	29	28	-2	6	22	25	2	-4	12	14	2	-7	17	13
4	-11	14	14	-2	4	24	25	2	-6	8	9	2	-8	25	25
4	-12	7	8	-2	2	33	34	1	1	7	8	1	-2	9	11
3	0	6	4	-2	0	35	39	1	0	34	36	1	-4	8	10
3	-1	6	7	-2	-1	6	3	1	-2	20	19	1	-6	13	15
3	-3	7	11	-2	-2	28	30	1	-3	7	4	0	1	6	10
3	-6	10	7	-2	-3	14	15	1	-4	7	3	0	0	21	20
3	-9	9	12	-3	6	24	29	1	-5	11	11	0	-1	16	19
2	0	34	36	-3	5	12	13	1	-6	27	25	0	-2	12	10
2	-2	29	29	-3	4	27	30	1	-8	29	29	0	-4	12	6
2	-3	9	13	-3	3	10	7	0	2	24	24	0	-5	9	10
2	-4	49	47	-3	2	15	16	0	0	42	42	0	-6	15	15
2	-5	9	7	-3	0	26	27	0	-2	44	44	-1	2	22	21
2	-6	37	36	-3	-1	6	2	0	-4	39	39	-1	0	35	34
2	-7	22	23	-3	-2	24	26	0	-5	10	11	-1	-2	37	40
2	-8	20	21	-4	5	9	7	0	-6	35	36	-1	-4	22	24
2	-9	9	10	-4	3	9	8	-1	2	14	11	-2	2	12	9
2	-10	31	33	-5	6	13	16	-1	0	16	12	-2	0	19	15
1	2	24	23	-5	5	7	10	-1	-2	18	20	-2	-2	14	16

Table 14. Molecular Weight Data

Complex	Actual M.W.	Solvent	Calibrant	Concentration (Formal, F)	Apparent M.W.	Time After Mixing (hours)
$[Cu(H\cdot DIIMINE)]_2$	495.46	$CHCl_3$	Benzil	0.02674	500.0	1
				0.06939	487.6	1
				0.02674	509.6	24
				0.06939	494.7	24
$[Ni(H\cdot DIIMINE)]_2$	485.84	$CHCl_3$	Benzil	0.02759	505.8	1
				0.06478	516.0	1
				0.06478	495.7	$2\frac{1}{2}$
				0.06478	479.8	120
$Co(DIIMINE)(ETAH)_2$	364.33	H_2O	NaCl	0.01164	108.8	1
		CH_3OH	Benzil	0.01123	248.5	1

the manufacturer.

Resistance readings for both calibrant and sample were taken after a predetermined amount of time had elapsed since the application of a drop of solution to the thermistor bead. This time interval was previously determined by observing the length of time required to stabilize the needle's movement. For chloroform, two minutes time was sufficient, while both water and methanol required a waiting period of five minutes.

N.M.R. Study

Table 15 shows the positions and relative intensities of the proton resonance frequencies observed for the complex $[Ni(H\cdot DIIMINE)]_2$. Spectra were obtained at room temperature on both Varian Model A60 and Jelco Model JNH-4H-100 n.m.r. instruments. Saturated solutions (0.04 $g\text{-}ml^{-1}$) of the nickel complex in $CDCl_3$ were used for all spectra recorded. Figure 4 (page 99) is an exploded view of the proton resonance signals observed between 6.52 and 7.60τ on the 100 MHz instrument.

Table 15. Summary of the 60 MHz N.M.R. Spectrum of the Complex $[Ni(H\cdot DIIMINE)]_2$

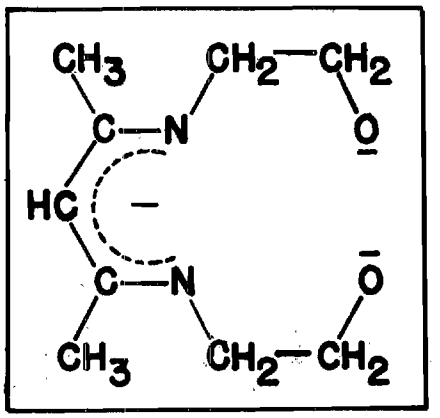
Assignment	Multiplicity	Position Relative to TMS[a]	Relative Intensity
O-H···O	singlet	11.83δ(-1.83τ)	1
H-C<	singlet	5.47δ(+4.53τ)	1
$-CH_2CH_2-$	multiplet	3.08δ(+6.95τ)	8
$-CH_3$	singlet	1.80δ(+8.20τ)	6

[a]TMS = tetramethylsilane

CHAPTER III

RESULTS AND DISCUSSION

Prior to this work, there had been relatively few reports of complexes containing diimines of 2,4-pentanedione (44-47), and no structural data were available from which reliable bond distances and angles could be obtained for these complexes. In this work, a cobalt(III) complex was prepared, and analytical data (ch. II, p. 17) indicated a compound of the formulation, $CoC_{13}H_{29}N_4O_4$, which could conceivably contain a diimine of 2,4-pentanedione as ligand. From this formulation, it could be reasoned that the coordinated groups consisted of a trinegative diimine group (7) and two neutral monodentate 2-aminoethanol groups. The



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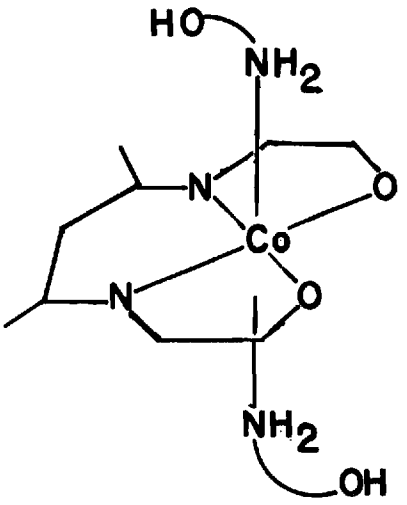
complex could then be postulated as (8). Another distinct possibility was that of (9) wherein 2-aminoethanol hydroxide groups have added across the imine linkages to give a complex containing a trinegative sexadentate ligand. Reactions of this nature had previously been observed for the



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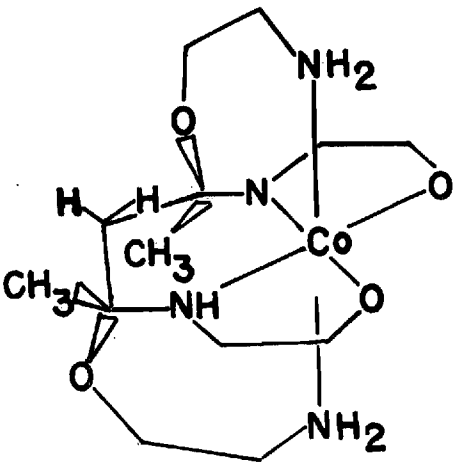

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TAAB[1] complexes of Ni(II) and Cu(II). In those cases, water (61), methanol (62), and N,N-bis(2-hydroxyethyl)methylamine (63) were added across the coordinated imine linkages.

In order to reconcile the structure of the complex to one of these two possible formulations (i.e. confirm the formation of the diimine ligand), a complete single crystal x-ray structure determination was per-

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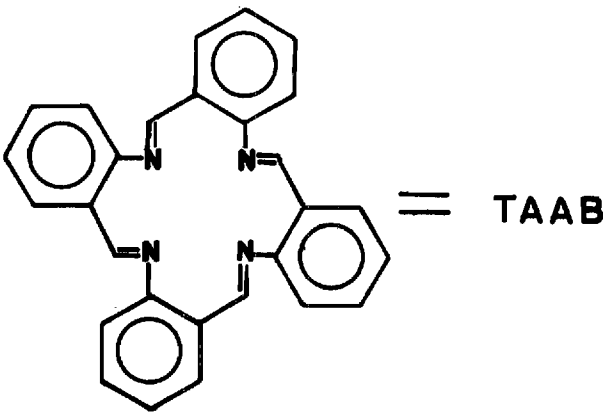
[1]TAAB = the planar tetradentate ligand formed from the self-condensation of four molecules of α-aminobenzaldehyde in the presence of certain transition metal ions, particularly Ni(II), Cu(II) and Zn(II).



= TAAB

formed. The results of this investigation corroborated the initial assumption; namely, that the complex consisted of a cobalt(III) ion octahedrally coordinated by a trinegative diimine ligand and two monodentate 2-aminoethanol groups. Figure 1 shows the asymmetric unit and Table 16 gives selected bond distances and angles for the structure.

The coordination geometry shows only small deviations from an octahedral arrangement of donor atoms about the cobalt. The cobalt-donor bond lengths range from 1.89Å to 1.98Å, while the angles at cobalt for cis-donor atoms vary between 85.5° and 94.6°. The diimine ligand fills four coplanar coordination sites and creates two five-membered and one six-membered chelate rings. Since the charge of the trivalent cobalt ion must be balanced by the loss of protons from the ligands, two protons appear to be lost from the oxygens, E10 and E20, and one proton is lost from carbon atom, AC3, which is beta to the two imine nitrogen atoms. This latter assumption (that a proton is lost from AC3) is based upon the fact that within the six-membered chelate ring, which includes both imine groups and AC3, the two carbon-carbon distances (AC3-AC4 and AC3-AC2) are equivalent (1.39(1)Å) and the two carbon-nitrogen distances (AC2-E1N and AC4-E2N) are equivalent (1.32(1)Å). In addition, the entire six-membered chelate ring, which includes both methyl groups attached to the imine carbons of the six-membered chelate ring, is essentially planar, as indicated by the distances of each atom from the least-squares plane of the coordinated atoms of the diimine ligand, Table 17. The only atom of the entire six-membered chelate ring that is more than 0.05Å out of the coordination plane of the cobalt is the methyl carbon, AC1, which is 0.19Å from the plane. Thus, there appears

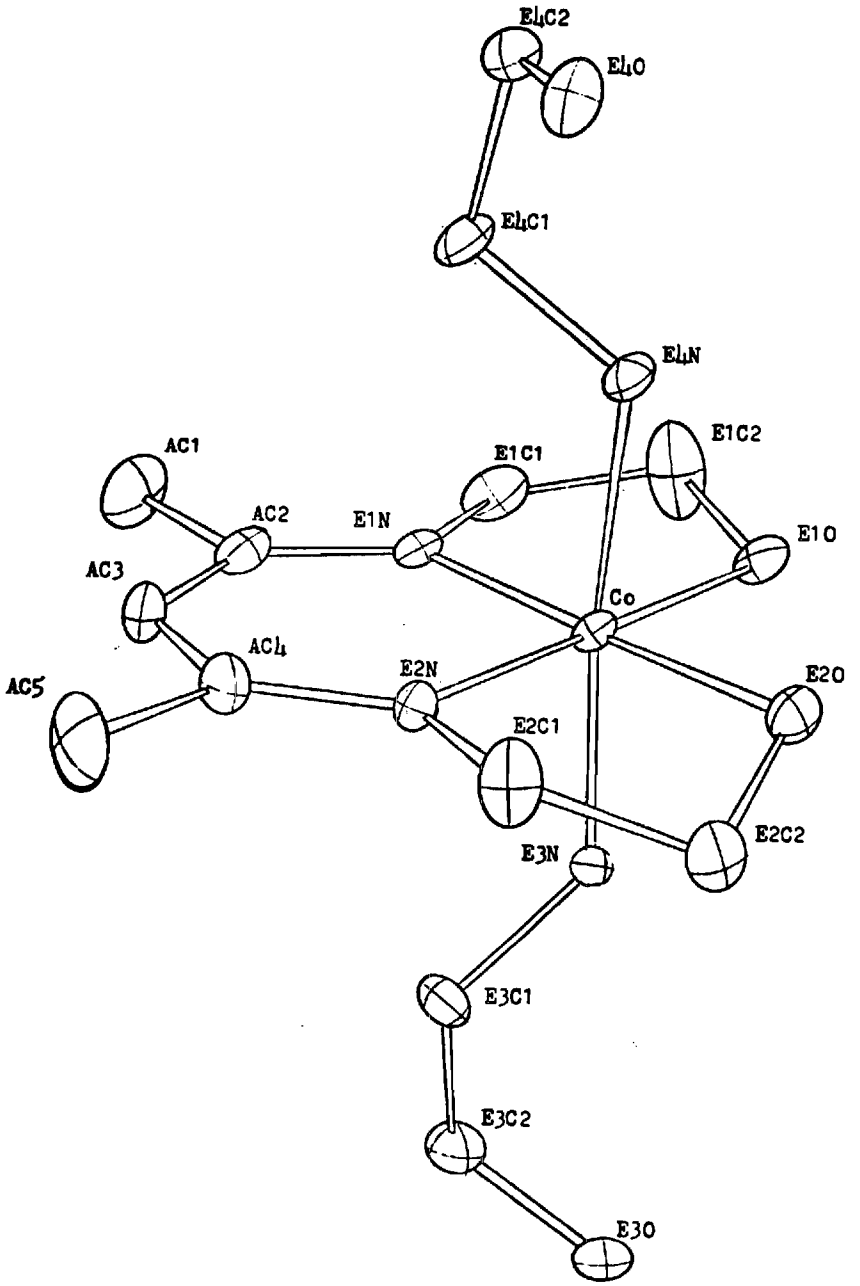


Figure 1. A Perspective Drawing of the Structure of Co(DIIMINE)$(ETAH)_2$

Table 16. Interatomic Distances (Å) and Angles (°) for Co(DIIMINE)(ETAH)$_2$

Atoms	Distance, Å	Atoms	Angles, °
Co - E1O	1.931(3)	E1O -Co -E1N	86.1(1)
Co - E2O	1.917(3)	E2O -Co -E2N	86.7(1)
Co - E1N	1.898(4)	E1O -Co -E2O	92.6(1)
Co - E2N	1.897(4)	E1N -Co -E2N	94.6(2)
Co - E3N	1.976(3)	E3N -Co -E1O	91.6(1)
Co - E4N	1.989(3)	E3N -Co -E1N	94.6(1)
E1O -E1C2	1.404(6)	E3N -Co -E2O	86.4(1)
E2O -E2C2	1.389(7)	E3N -Co -E2N	89.8(1)
E3O -E3C2	1.402(6)	E4N -Co -E1O	85.5(1)
E4O -E4C2	1.421(6)	E4N -Co -E1N	91.3(2)
E1N -E1C1	1.478(6)	E4N -Co -E2O	87.6(1)
E2N -E2C1	1.458(6)	E4N -Co -E2N	93.0(1)
E3N -E3C1	1.495(5)	E1O -Co -E2N	178.3(2)
E4N -E4C1	1.486(5)	E2O -Co -E1N	178.4(2)
E1C1 -E1C2	1.520(8)	E3N -Co -E4N	173.3(1)
E2C1 -E2C2	1.460(9)	Co -E2O -E2C2	110.1(3)
E3C1 -E3C2	1.504(6)	Co -E1O -E1C2	108.4(3)
E4C1 -E4C2	1.505(6)	Co -E3N -E3C1	121.1(3)
AC2 -AC3	1.399(7)	Co -E4N -E4C1	121.8(3)
AC3 -AC4	1.392(8)	Co -E1N -E1C1	112.1(3)
AC1 -AC2	1.523(6)	Co -E2N -E2C1	112.8(3)
AC4 -AC5	1.518(6)	Co -E1N -AC2	126.4(3)
E1N -AC2	1.324(6)	Co -E2N -AC4	126.1(3)
E2N -AC4	1.327(6)	E1O -E1C2 -E1C1	109.6(4)
E3O -E2O'	2.679(5)	E2O -E2C2 -E2C1	116.4(5)
E4O -E1O''	2.593(4)	E3O -E3C2 -E3C1	114.1(4)
		E4O -E4C2 -E4C1	112.4(3)
		E1C2 -E1C1 -E1N	106.2(4)
		E2C2 -E2C1 -E2N	109.1(4)

Table 16. (Continued)

Atoms	Angles, °	Atoms	Angles, °
E3C2 -E3C1 -E3N	113.7(3)	E4C2 -E4C1 -E4N	112.1(3)
E1N -AC2 -AC1	119.4(5)	E2N -AC4 -AC5	119.3(5)
E1N -AC2 -AC3	123.0(4)	E2N -AC4 -AC3	123.3(4)
AC1 -AC2 -AC3	117.6(4)	AC5 -AC4 -AC3	117.4(4)
AC2 -AC3 -AC4	126.5(4)	AC2 -E1N -E1C1	121.3(4)
AC4 -E2N -E2C1	121.0(4)		

Table 17. Equation of the Least-Squares Plane[a] of the Coordinated Atoms of the Diimine Ligand and Distances of Atoms from this Plane for the Complex, $Co(DIIMINE)(ETAH)_2$

Equation of the Least-Squares Plane for E1O, E2O, E1N and E2N:

$$0.022X - 0.008Y + 1.000Z + 1.819 = 0$$

Atom	Distance From Plane, Å	Atom	Distance From Plane, Å
Co	0.021	E2C1	0.054
AC1	-0.190	E2C2	-0.234
AC2	-0.054	E2N	-0.004
AC3	-0.027	E3O	4.883
AC4	0.001	E3C1	2.829
AC5	0.036	E3C2	4.283
E1O	-0.004	E3N	1.981
E1C1	-0.080	E4O	-4.345
E1C2	0.489	E4C1	-2.821
E1N	0.004	E4C2	-4.237
E2O	0.004	E4N	-1.952

[a]The equation is referred to orthogonal axes with the orthogonal X axis coincident to a and the orthogonal Z axis coincident to c^*.

to be complete delocalization of negative charge about a π-system within the six-membered chelate ring and, therefore, good evidence for proton loss from carbon atom, AC3.

In comparing structural parameters between corresponding atoms in the two halves of the diimine ligand (i.e. the two five-membered chelate rings), one can discern some interesting distinctions. For instance, while most of the thirteen atoms of the diimine ligand are coplanar and in the coordination plane of the cobalt, the carbon atoms, E1C2 and E2C2, (corresponding atoms in the two different five-membered rings) are on opposite sides of the plane and show much larger deviations from the plane, +0.49Å and -0.23Å, respectively.[2] Finally, when comparing bond distances between corresponding atoms in the two rings, only one pair of bond distances shows a difference greater than three times the standard deviation; the carbon-carbon distances in the five-membered rings differ by 0.060Å which is greater than seven times their standard deviations.

The two monodentate 2-aminoethanol groups occupy trans-positions and, since amine groups are generally better ligands than alcohols, they are assumed to be coordinated through nitrogen. With this assignment, the carbon-nitrogen distances (1.50 and 1.48Å) and the carbon-oxygen distances (1.40 and 1.42Å) are consistent with values found for the carbon-nitrogen distances (1.47 and 1.46Å) and the carbon-oxygen distances (1.40 and 1.38Å) of the five-membered chelate rings. The fact

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[2]A plus (+) sign indicates that the atom is above the defined plane, while a minus (-) sign indicates that the atom is below the defined plane.

that the temperature factors of these atoms were normal is further support for the assignment.

The non-coordinated alcohol groups of the 2-aminoethanol ligands and the alkoxide oxygens of adjacent molecules are involved in hydrogen bonding. Infinite chains are created by the interaction of one alcohol group, E30, with the alkoxide, E20, of the molecule related by the inversion center at the origin and by interaction of the second alcohol group, E40, with the alkoxide, E10, of the molecule related by the inversion center at $0,-\frac{1}{2},-\frac{1}{2}$. The oxygen-oxygen distances, 2.68(1)Å and 2.59(1)Å, respectively, indicate reasonably strong hydrogen bonding. Figure 2 shows the hydrogen bonded chains running through the lattice parallel to the *bc* plane.

The isolation of a cobalt(III) complex containing the diimine of 2,4-pentanedione and 2-aminoethanol raised questions as to the nature of complexes that might be prepared with other metal ions. What kind of complexes could one expect with divalent metal ions? Since the diimine ligand could lose three protons, would the complexes be anionic or neutral? Would strong hydrogen bonding be observed as in the cobalt(III) complex? Most importantly, would any of the divalent metal complexes of the diimine ligand exhibit interesting magnetic properties?

With these questions in mind, an effort was made to prepare the nickel(II) and copper(II) complexes of N,N'-bis(2-hydroxyethyl)-2,4-pentanediimine. Numerous attempts failed at first because care was not taken in heating the reaction mixtures (ch. II, p. 18). Extensive heating of the nickel(II) mixture would not lead to a precipitate, even on long standing; and, extensive heating of the copper(II) mixture would

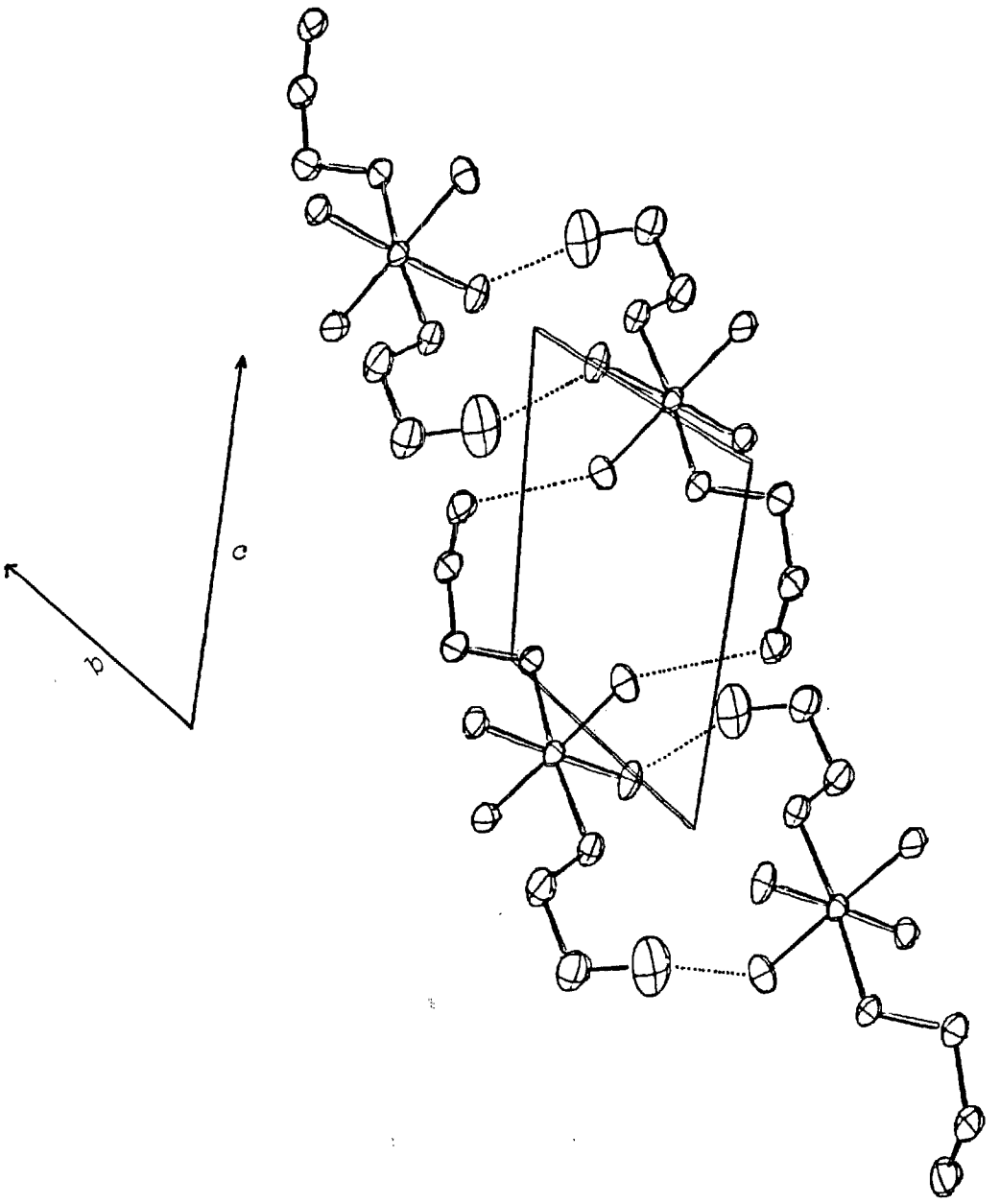

Figure 2. Hydrogen-Bonded Chains in Co(DIIMINE)$(ETAH)_2$

cause the precipitation of a copper mirror. Nevertheless, by gently heating the reaction mixtures to 115°C, it was possible to isolate green microcrystalline samples of both the nickel(II) and copper(II) complexes. Analysis of these compounds indicated an empirical formula for the ligand, $C_9H_{16}N_2O_2$, which was consistent with the assumption that the ligand was the dinegative diimine, $(H\cdot DIIMINE)^{2-}$. At first, little interest was generated by this discovery because it appeared that the complexes were simply monomers of the formulation, M(H·DIIMINE). Fortunately, a routine measurement of the density of the nickel(II) complex by the flotation method followed by a measurement of the crystallographic cell parameters by single crystal x-ray diffraction techniques revealed an interesting feature of the compound. In order to make the density measurement agree with that calculated from the x-ray data, one had to assume that the unit cell contained four formula units of the type, Ni(H·DIIMINE). The question was raised that since each formula unit was inherently asymmetric, was it likely that <u>four</u> independent asymmetric formula units were packed into a space group of symmetry P1? Or, was it more likely that some clustering of formula units had occurred to allow packing into space group $P\bar{1}$? If clustering had occurred, what kind of cluster was it? Finally, would this green diamagnetic nickel complex contain octahedrally coordinated nickel ions, as is generally characteristic of green nickel complexes, or would the nickel ions be coordinated in a square-planar fashion, as is often the case for diamagnetic nickel complexes? One way to answer these questions was to determine the molecular structure.

Since nice crystals of the nickel(II) diimine complex had been

isolated on the first attempted recrystallization from toluene, a single crystal was chosen for collection of the intensity data. While data on the nickel complex was being measured, crystals of a copper diimine complex were obtained, their density determined by flotation, and unit cell parameters measured on the precession camera. Due to the way that the crystal of the copper diimine complex had been mounted on the glass fiber, the unit cell parameters were not the same as those previously observed for the nickel diimine complex, and it appeared as though the two complexes were not isomorphous[3]. On the other hand, the density, the number of formula units per unit cell, the symmetry of the space group, and the volume of the unit cell agreed quite well with those observed for the nickel complex. Consequently, the same questions could be raised concerning the structure of the copper diimine complex as were raised previously of the nickel diimine complex.

Pursuant to these results, magnetic susceptibility measurements were made on both the nickel and copper complexes. The nickel complex showed only a negligible room temperature magnetic moment of 0.37 B.M., and this was believed to be due, in part, to the presence of a slight amount of paramagnetic impurity and, in part, to the inadequate quenching of orbital contributions to the magnetic moment. The copper complex showed a "normal" room temperature magnetic moment ($\mu_{eff}^{298^\circ K}$ = 1.69 B.M.), but on lowering the temperature the moment dropped considerably, ($\mu_{eff}^{193^\circ K}$ = 1.56 B.M. and $\mu_{eff}^{77^\circ K}$ = 1.14 B.M.; ch. II, pp. 28-30). Clearly,

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[3]A Delaunay reduction carried out some time later did show that the complexes were isomorphous and possessed identical structures.

there appeared to be some pathway available for magnetic exchange coupling in the copper(II) diimine complex. This deduction made it most imperative that a structure for the copper(II) complex be determined also. Consequently, a good single crystal of the copper complex was chosen, mounted on a glass fiber, and aligned on the diffractometer in preparation for collection of intensity data.

While data on the copper complex was being collected, work was begun on solving the nickel(II) diimine structure with the intensity data that had been collected earlier. The structure was solved by methods already described (ch. II, p. 36). The structure obtained from the first electron density map is shown in Figure 3. Selected bond distances and angles for the nickel structure are shown in Table 18.

The structure can be described as containing dimeric units of the formulation, $[Ni(H\cdot DIIMINE)]_2$. There are two such dimeric units per unit cell with each dimeric unit occupying an inversion center in the space group, $P\bar{1}$. The first dimeric unit was arbitrarily positioned at the inversion center at 0,0,0; and, the second dimeric unit was necessarily positioned at the inversion at $0,0,\frac{1}{2}$. The dimers are held together by strong hydrogen bonds as evidenced by the exceedingly short oxygen-oxygen distances (O2-O1' and O1-O2') of 2.34(2)Å in dimer unit 1 and 2.33(2)Å in dimer unit 2. In fact, the only other hydrogen bond that is known to be shorter than these is the F-H-F bond found in $NaHF_2$ (64) with a F-F contact of 2.264(3)Å.

The coordination geometry about the nickel ion does not deviate greatly from an ideal square-planar geometry. This is evidenced by the observations that in both dimeric units the nickel-donor atom distances

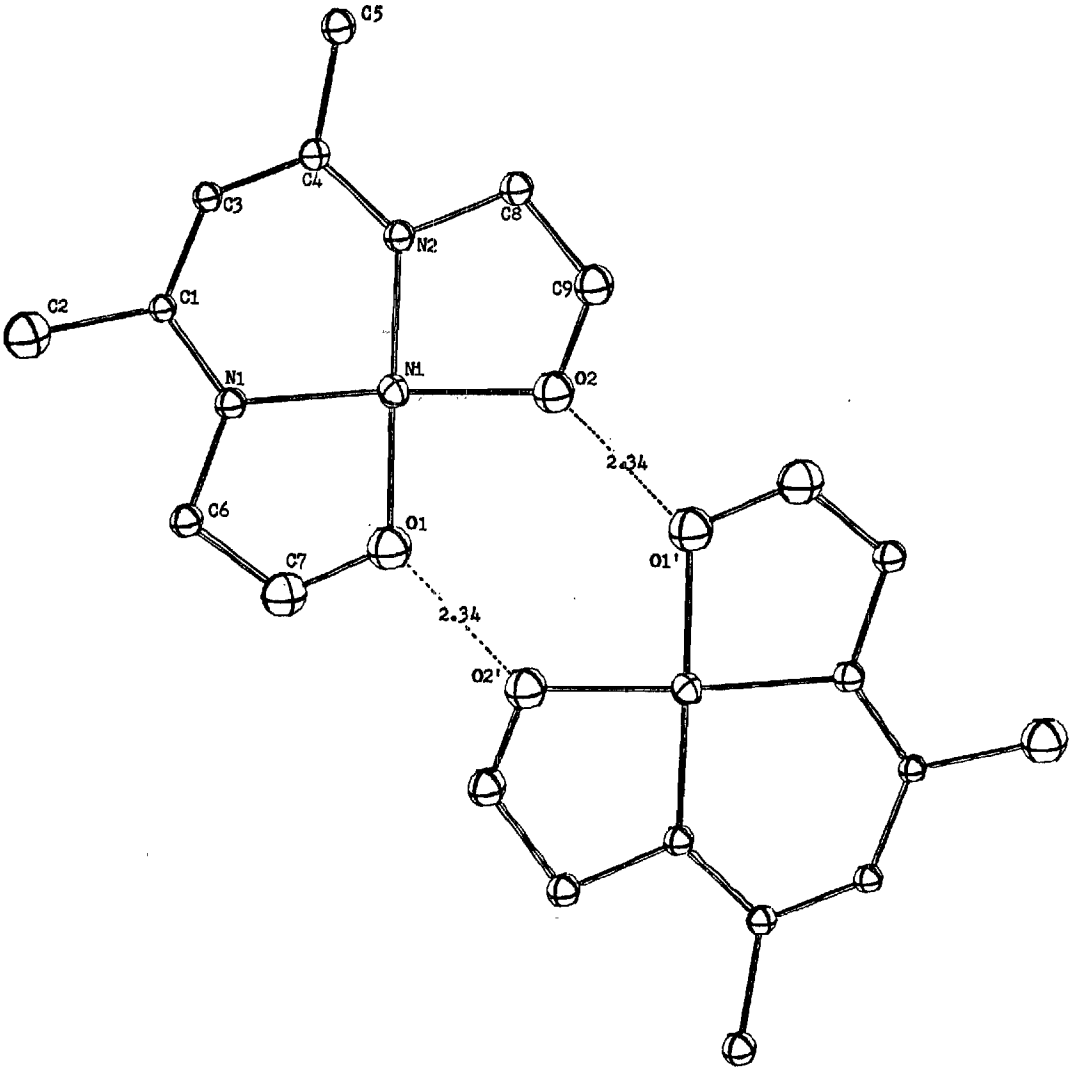

Figure 3. A Perspective Drawing of the Structure of $[Ni(H\cdot DIIMINE)]_2$

Table 18. Interatomic Distances (Å) and Angles (°) for the Divalent Metal Diimine Complexes, $[M(H\cdot DIIMINE)]_2$

	$[Ni(H\cdot DIIMINE)]_2$ Distance, Å		$[Cu(H\cdot DIIMINE)]_2$ Distance, Å	
Atoms	Unit 1	Unit 2	Unit 1	Unit 2
M-M[a]	4.99(1)	4.98(1)	4.980(6)	4.978(6)
M-O1	1.86(2)	1.86(2)	1.94(1)	1.93(1)
M-O2	1.90(2)	1.87(2)	1.96(1)	1.94(1)
M-N1	1.86(2)	1.84(2)	1.87(1)	1.91(1)
M-N2	1.81(2)	1.84(2)	1.90(1)	1.91(1)
O1-C7	1.40(3)	1.37(3)	1.43(2)	1.38(2)
O2-C9	1.38(3)	1.43(3)	1.43(2)	1.44(2)
N1-C6	1.51(3)	1.53(3)	1.49(2)	1.50(2)
N1-C1	1.32(2)	1.30(2)	1.31(1)	1.28(2)
N2-C8	1.51(3)	1.44(3)	1.47(2)	1.49(2)
N2-C4	1.37(2)	1.32(3)	1.32(1)	1.24(2)
C6-C7	1.45(3)	1.51(4)	1.49(2)	1.51(2)
C8-C9	1.52(3)	1.49(3)	1.58(2)	1.52(2)
C1-C2	1.53(3)	1.54(3)	1.62(2)	1.61(2)
C4-C5	1.52(3)	1.52(3)	1.57(2)	1.63(2)
C1-C3	1.34(3)	1.42(4)	1.38(2)	1.38(2)
C3-C4	1.41(3)	1.40(3)	1.35(2)	1.40(2)
O1-O2'[b]	2.34(2)	2.33(2)	2.30(1)	2.28(1)
	Angles, °		Angles, °	
Atoms	Unit 1	Unit 2	Unit 1	Unit 2
O1-M-O2	88.7(8)	89.2(7)	92.6(5)	92.2(6)
O1-M-N1	86.8(8)	89.4(7)	86.2(6)	87.8(5)
N1-M-N2	95.8(7)	94.7(7)	95.0(6)	93.3(6)
N2-M-O2	88.5(7)	96.2(7)	86.0(5)	86.5(5)

Table 18. (Continued)

Atoms	$[Ni(H\cdot DIIMINE)]_2$ Angles, ° Unit 1	Unit 2	$[Cu(H\cdot DIIMINE)]_2$ Angles, ° Unit 1	Unit 2
M-O1-C7	110.9(15)	109.1(15)	111.1(12)	111.0(13)
O1-C7-C6	116.8(21)	117.1(22)	114.9(18)	117.3(19)
C7-C6-N1	104.5(18)	105.2(17)	107.6(16)	108.4(15)
C6-N1-M	114.0(12)	112.6(12)	115.4(11)	112.7(10)
C6-N1-C1	120.3(16)	119.6(15)	119.2(14)	121.1(14)
M-N1-C1	124.6(14)	127.5(12)	124.7(12)	125.8(11)
N1-C1-C2	119.6(18)	117.6(16)	117.3(15)	117.4(15)
N1-C1-C3	122.5(19)	124.0(21)	123.6(18)	125.1(17)
C2-C1-C3	117.7(19)	118.2(22)	118.9(17)	117.4(17)
C1-C3-C4	131.0(22)	122.4(26)	128.1(22)	122.9(18)
C3-C4-C5	122.0(18)	116.9(20)	119.9(18)	113.4(16)
C3-C4-N2	116.0(19)	124.6(20)	121.9(18)	127.0(17)
C5-C4-N2	121.6(18)	119.4(18)	118.0(15)	119.4(17)
C4-N2-M	129.4(14)	127.2(14)	125.8(12)	125.3(12)
C4-N2-C8	116.0(15)	119.4(16)	119.0(14)	122.2(15)
M-N2-C8	114.3(12)	113.2(13)	114.2(11)	112.3(10)
N2-C8-C9	101.5(15)	111.7(16)	104.5(14)	111.4(15)
C8-C9-O2	114.4(17)	108.1(16)	108.7(14)	109.6(16)
M-O2-C9	105.3(13)	111.8(13)	108.6(10)	111.4(11)

[a] M represents the metal atom appropriate to the complex listed.

[b] O2' refers to the oxygen atom related to O2 by inversion through 0,0,0 in Unit 1 or by inversion through $0,0,\frac{1}{2}$ in Unit 2.

range from 1.81 to 1.90Å, the angles at nickel for cis-donor atoms range from 88.5° to 95.8° and the nickel atoms are less than 0.07Å out of the coordination plane of the donor atoms. In fact, Table 19 indicates that all the atoms in the six-membered chelate rings, which consist of the two imine groups and carbon, C3, do not deviate by more than 0.13Å from the coordination plane of the donor atoms. Since the carbon-nitrogen distances (C1-N1 and C4-N2) are equivalent to within 2σ (1.32(8)Å) and the carbon-carbon distances (C1-C3 and C3-C4) are equivalent to within 2σ (1.39(6)Å), there is strong evidence here, as there was in the case of the cobalt(III) complex, that there is delocalization of negative charge in the π-system of the six-membered chelate ring.

A further comparison of the ligand geometries in the nickel(II) and cobalt(III) complexes, reveals that in both cases, the bond distances within the ligand are of comparable magnitude, and the atoms which deviate most from the coordination plane are the methyl groups attached to the imine carbons of the six-membered chelate ring and the carbon atoms adjacent to the donor oxygen atoms. On the other hand, the methylene carbons of unit 2, adjacent to the donor oxygen atoms, are on the same side of the coordination plane while in unit 1 and in the cobalt complex described earlier they are on opposite sides of the coordination plane. Other than this, the ligand geometries for both the nickel(II) and cobalt(III) complexes are equivalent.

Of course the most peculiar aspect of the nickel(II) structure for which there is no analogy in the cobalt(III) structure is the dimeric clustering brought on by the strong hydrogen bonding between donor oxygen atoms. Since the diimine group in each monomeric portion of the

Table 19. Equations for the Least-Squares Plane[a] of the Coordinated Atoms of the Diimine Ligand and Distances of Atoms from These Planes for the Divalent Metal Diimine Complexes

Equations of the Least-Squares Plane for N1, N2, O1 and O2 in:

$[Ni(H\cdot DIIMINE)]_2$

Unit 1: $0.475X - 0.323Y + 0.818Z - 0.249 = 0$

Unit 2: $-0.424X + 0.427Y + 0.798Z - 6.067 = 0$

$[Cu(H\cdot DIIMINE)]_2$

Unit 1: $0.481X - 0.288Y + 0.824Z - 0.232 = 0$

Unit 2: $-0.416X + 0.400Y + 0.815Z - 6.161 = 0$

	$[Ni(H\cdot DIIMINE)]_2$ Distance from Plane, Å		$[Cu(H\cdot DIIMINE)]_2$ Distance from Plane, Å	
Atom	Unit 1	Unit 2	Unit 1	Unit 2
M[b]	-0.036	0.070	-0.002	0.024
O1	-0.020	-0.009	-0.016	-0.006
O2	0.013	0.009	0.011	0.006
N1	0.017	0.008	0.015	0.006
N2	-0.015	-0.009	-0.013	-0.006
C1	-0.035	-0.029	-0.028	-0.104
C2	-0.114	-0.108	-0.114	-0.212
C3	0.011	-0.062	0.056	-0.147
C4	0.017	-0.109	0.071	-0.121
C5	0.194	-0.269	0.295	-0.291
C6	-0.121	0.119	-0.124	-0.006
C7	0.216	0.384	0.162	0.203
C8	0.053	0.118	0.114	0.042
C9	-0.445	0.486	-0.472	0.454

[a]The equations are referred to orthogonal axes with the orthogonal X axis coincident to a and the orthogonal Z axis coincident to c^*.

[b]M represents the metal atom appropriate to the complex listed.

nickel(II) complex loses one proton from the carbon atom adjacent to the imine linkages and one proton from an alcoholic oxygen, one alcoholic proton remains attached and is then available for hydrogen-bonding to another monomer. This hydrogen bonding between monomers does not give rise to a single kind of dimeric unit, however; one dimeric unit is closer to planarity than the other. The dihedral angles between the coordination plane of the nickel(II) and the plane consisting of the hydrogen-bonded oxygens are approximately 12.04° for unit 1 while in unit 2 the angle is only 1.23°. Table 20 gives the deviations of each atom from the least-squares plane of the hydrogen-bonded oxygen atoms for each of the two asymmetric units in the structure.

Having observed that strong hydrogen bonding was responsible for the formation of dimers in the structure of the nickel(II) diimine complex, it was speculated that hydrogen-bonded dimers might also be present in the copper(II) diimine structure. This further prompted the structure determination of the copper(II) diimine complex. The structure turned out to be identical to that observed for the nickel(II) diimine complex. Earlier doubts as to the equivalence of the two structures were immediately dissipated once the Delaunay reduced cell parameters were compared. Tables 18-20, referred to earlier, also include the relevant structural parameters for the copper(II) structure. The tables were constructed in this manner so as to provide an easy means of comparing the two structures.

The same types of anomalies in the ligand geometry are present in the copper(II) structure as were observed in the nickel(II) structure. For one, the atoms which deviate by more than 0.15Å from the

Table 20 Equations for the Least-Squares Plane[a] of the Hydrogen-Bonded Oxygen Atoms and Distances of Atoms from the Plane for the Divalent Metal Diimine Complexes

Equations of the Least-Squares Plane for O1, O2, O1'[b] and O2'[c] in:

$[Ni(H\cdot DIIMINE)]_2$

Unit 1: $-0.334X + 0.478Y - 0.811Z + 0.000 = 0$
Unit 2: $-0.428X + 0.431Y + 0.793Z - 6.068 = 0$

$[Cu(H\cdot DIIMINE)]_2$

Unit 1: $-0.349X + 0.446Y - 0.823Z - 0.000 = 0$
Unit 2: $-0.462X + 0.345Y + 0.816Z - 6.406 = 0$

	$[Ni(H\cdot DIIMINE)]_2$ Distance from Plane, Å		$[Cu(H\cdot DIIMINE)]_2$ Distance from Plane, Å	
	Unit 1	Unit 2	Unit 1	Unit 2
M[d]	0.310	0.071	0.264	-0.071
O1	0.000	0.000	0.000	0.000
O2	0.000	0.000	0.000	0.000
N1	0.492	0.019	0.481	-0.177
N2	0.565	-0.017	0.541	-0.200
C1	0.818	-0.019	0.781	-0.378
C2	1.064	-0.088	1.033	-0.546
C3	0.913	-0.060	0.831	-0.472
C4	0.815	-0.116	0.714	-0.401
C5	0.843	-0.284	0.683	-0.645
C6	0.477	0.139	0.494	-0.141
C7	-0.134	0.403	-0.069	0.173
C8	0.398	0.100	0.317	-0.113
C9	0.583	0.468	0.595	0.400

[a] The equations are referred to orthogonal axes with the orthogonal X axis coincident to a and the orthogonal Z axis coincident to c^*.

[b] O1' refers to the oxygen atom related to O1 by inversion through 0,0,0 in Unit 1 or by inversion through $0,0,\frac{1}{2}$ in Unit 2

[c] O2' refers to the oxygen atom related to O2 by inversion through 0,0,0 in Unit 1 or by inversion through $0,0,\frac{1}{2}$ in Unit 2

[d] M represents the metal atom appropriate to the complex listed.

coordination plane of the metal are the methyl groups attached to the six-membered chelate rings, and the methylene carbons adjacent to the donor oxygen atoms. Secondly, these same methylene groups are on opposite sides of the coordination plane in unit 1, but are on the same side of the coordination plane in unit 2.

The coordination geometry about copper shows only small deviations from an ideal square-planar geometry. The copper-donor atom distances range between 1.87Å and 1.96Å; the angles at copper for cis-donor atoms vary between 86.0° and 95.0°; and, the copper(II) ions are less than 0.03Å away from the plane of the donor atoms. In addition, there is good evidence for a delocalization of negative charge within the π-framework of the six-membered chelate ring. Within a given dimer, the carbon-carbon distances, C1-C3 and C3-C4, are equivalent to within 2σ. On the other hand, the carbon-nitrogen distances (C4-N2) in unit 1 of 1.32(1)Å is more than 8σ longer than the 1.24(1)Å found in unit 2. Similar comparisons between the asymmetric units, however, reveal that no other corresponding bond distances differ by more than 3σ. Finally, the dihedral angle between the coordination plane of the metal and the plane containing the hydrogen-bonded oxygen atoms of the dimer is 11.40° in unit 1 and only 4.13° in unit 2.

Despite these minor structural dissimilarities between units 1 and 2 of the copper(II) diimine structure, both units show remarkably similar hydrogen-bonded oxygen contacts of 2.30(1)Å and 2.28(1)Å, respectively. These contacts are also similar to those found in the nickel(II) diimine structure (2.34(2)Å and 2.33(2)Å). In light of these exceedingly short oxygen-oxygen contacts, and hence, exception-

ally strong hydrogen bonds, a reasonable explanation for the apparent antiferromagnetic behavior of the copper complex suggests itself. Since the intradimer copper-copper separations of nearly 5Å exclude any possibility of direct exchange between metal ions (i.e. direct metal-metal bonding), and since the interdimer separations of nearly 6Å exclude any cooperative magnetic interactions between dimers (i.e. interclusteral antiferromagnetism), the antiferromagnetic behavior of the complex must be due to superexchange coupling between copper ions, proceeding via a pathway that includes the bridging hydrogen atoms. Since hydrogen atoms have only s-orbitals of sufficiently low energy, the pathway for superexchange is entirely σ in character (i.e. the overlap of atomic orbitals constituting the exchange pathway are all of the σ-type). In fact, this is the first example of its kind wherein a good estimate may be made of the s-orbital contribution to the total effectiveness of a superexchange mechanism. In order to test the strength of the hydrogen bonds holding the dimers together, known amounts of the nickel(II) or copper(II) dimers were dissolved in chloroform and molecular weight measurements were taken at various intervals of time (ch. II, p. 75). The results shown in Table 14 indicate that only minimal dissociation of the dimers occurred in freshly prepared solutions. Solutions of the cobalt(III) complex were also studied, and the data clearly indicates appreciable dissociation of the complex. This dissociation probably corresponds to the simultaneous loss of both monodentate 2-aminoethanol groups, thus indicating weaker hydrogen bonding in the solid than in solution. This deduction is supported to some extent by the fact that less dissociation occurs in methanol solutions than in water.

for x-ray work have not as yet been obtained from either of the reaction mixtures or from numerous attempts at recrystallization. Nevertheless, magnetic measurements have been made on these compounds at room temperature and at liquid nitrogen temperature. The compound with the formulation, Ni_2(DIIMINE)(OH), has a magnetic moment per formula unit of 3.09 B.M. at 298°K and 2.90 B.M. at 77°K (ch. II, pp. 31-32), while the compound, Ni_3(DIIMINE)$_2$(ETAH)$_4$, has a magnetic moment per formula unit of 3.09 B.M. at 297°K and 2.92 B.M. at 77°K (65). These data clearly indicate that both complexes contain only one paramagnetic nickel(II) ion per formula unit. Since the remaining nickel(II) ions in either complex must be diamagnetic and since square-planar nickel(II) complexes are invariably diamagnetic, the diamagnetic nickel(II) ions of both complexes are assumed to be coordinated in a square-planar geometry. Further speculations as to the structures of these complexes will be delayed until Chapter IV.

Since little dissociation was observed in freshly prepared chloroform solutions of the nickel(II) diimine complex, an n.m.r. spectrum might be used to detect the signal due to the bridging hydrogen atoms. With this in mind, n.m.r. spectra were recorded on both 60 and 100 MHz instruments, and the results tabulated in Table 15. The bridging hydrogen was observed as a broad band near -1.83τ and integrated in the correct ratio to the other signals in the spectrum. One interesting feature of the spectrum is the set of resonance lines observed between 6.52 and 7.60τ shown in Figure 4. These absorptions are interpreted as being due to the methylene hydrogens in the five-membered chelate rings. Due to the thermal motion above and below the coordination plane of the nickel, both hydrogens on a given methylene carbon become magnetically equivalent at room temperature. This can result in what n.m.r. spectroscopists term an A_2B_2 or A_2X_2 spin-coupled pattern. Although these systems are extremely difficult to analyze numerically, their most recognizable feature is the mirror symmetry of the resonance signals. As Figure 4 clearly shows, a mirror of symmetry does exist in the resonance signals due to the $-CH_2-CH_2-$ grouping. Further support for this assignment comes from the fact that the pseudo-coupling constants abstracted from the 60 and 100 MHz spectra are not equal, but are field dependent. Consequently, the coupling observed is something other than simple first-order. In addition, the ratio of peak heights in the multiplet is not in the correct ratio for simple first-order coupling.

Structural determinations on the other complexes of N,N'-bis(2-hydroxyethyl)-2,4-pentanediimine, namely, $Ni_3(DIIMINE)_2(ETAH)_4$ and $Ni_2(DIIMINE)(OH)$, could not be done because single crystals suitable

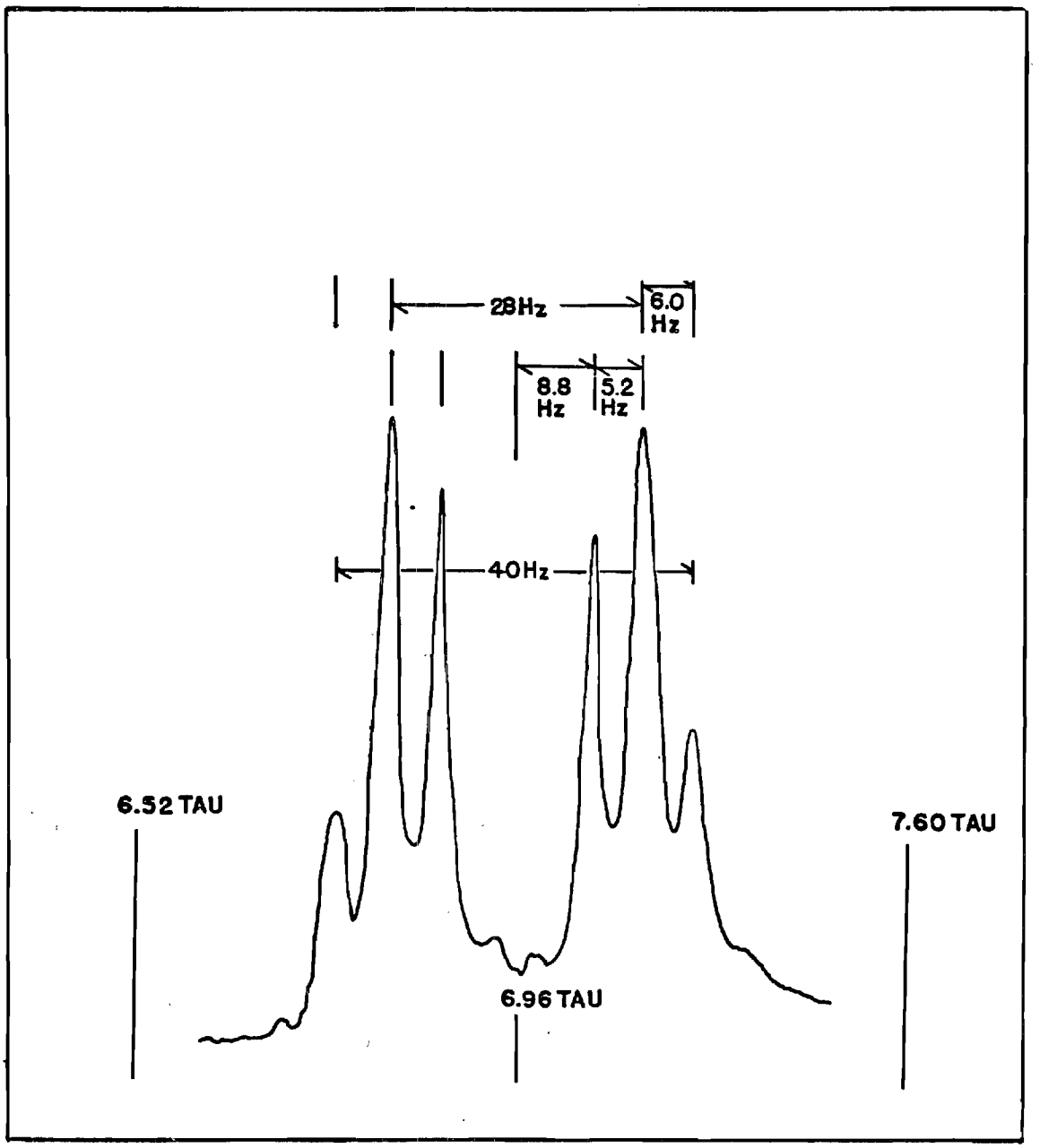

Figure 4. 100 MHz N. M. R. Spectrum for $[Ni(H\cdot DIIMINE)]_2$ in the Region 6.52 - 7.60 τ

CHAPTER IV

CONCLUSIONS

Prior to this work it was well known that the copper(II) complexes of the monoimine of 2,4-pentanedione and 2-aminoethanol, $[Cu(EIA)]_4$, and 3-amino-1-propanol, $[Cu(PIA)]_2$, had distinctly different molecular structures and exhibited drastically different magnetic behavior. This anomaly prompted a study of complexes that might be formed from the 1:2 condensation of 2,4-pentanedione with 2-aminoethanol; namely, the complexes of the ligand N,N'-bis(2-hydroxyethyl)-2,4-pentanediimine. In this study, a series of five different complexes have been prepared and the structures of three of these have been determined. Of the three structures reported, all contain the tetradentate diimine ligand which occupies four coordination positions in a nearly square-planar arrangement. In all cases, the ligand appears to have lost a proton from the carbon atom adjacent to the imine linkages in the six-membered chelate ring and one or more protons from the alcoholic oxygens of the five-membered chelate rings.

The structure of the cobalt(III) complex, $Co(DIIMINE)(ETAH)_2$, was the first of a series to be studied. Although the complex itself did not exhibit any interesting magnetic properties, its molecular structure did serve to verify the presence of the diimine ligand in the complex. In addition, an interesting framework of hydrogen-bonded chains was observed in the solid state.

The structures of the nickel(II) and copper(II) diimine complexes were shown to be isomorphous and to contain discrete dimers held together by cooperative hydrogen bonding. The intradimer hydrogen bonding was exceedingly strong as evidenced by the short oxygen-oxygen contact of approximately 2.30Å in both complexes. This is the shortest oxygen-oxygen contact and hence the strongest hydrogen bond ever reported between oxygen atoms. The only other hydrogen bond known to be shorter is that between hydrogen and fluorine in the compound, $NaHF_2$ (64) where the F-H-F distance is 2.264(3)Å. Molecular weight studies indicated that both the nickel(II) and copper(II) hydrogen-bonded dimers did not dissociate appreciably in freshly prepared chloroform solution.

Although the copper(II) and nickel(II) diimine complexes are not the first hydrogen-bonded dimers reported, they constitute the first examples of edge-shared hydrogen-bonded dimers[1]. On the other hand, the copper(II) dimer is the first hydrogen-bonded dinuclear complex exhibiting magnetic exchange interactions between metal ions. The antiferromagnetic interaction is believed to occur by a superexchange mechanism via a σ-pathway through the bridging hydrogens. Direct exchange between copper ions is ruled out due to the large metal-metal separation of 4.98Å. Interdimer interactions can also be ruled out because the dimers are well separated from one another.

The two other nickel complexes that were prepared could not be

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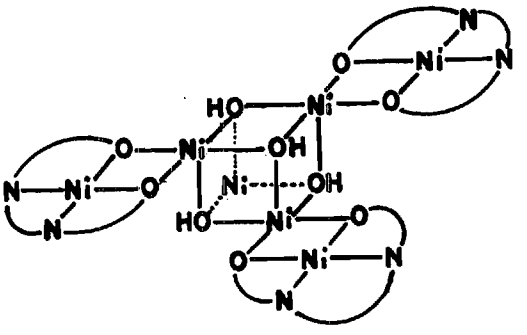
[1]The complex, $CoNi(ETA)_3(ETAH)_3I_2$, (48) consists of octahedral trischelates of cobalt(III) and nickel(II) held together by three hydrogen bonds between the oxygen faces of the two octahedra with an oxygen-oxygen distance of 2.51Å.

studied by x-ray diffraction because suitably large single crystals could not be obtained. The complex, Ni_2(DIIMINE)(OH), has a room temperature moment of 3.09 B.M. per formula unit, which corresponds to one paramagnetic nickel(II) ion and one diamagnetic nickel(II) ion per formula unit. At liquid nitrogen temperature, the moment is 2.90 B.M. per formula unit and again corresponds to one paramagnetic nickel(II) ion and one diamagnetic nickel(II) ion per formula unit. By analogy, the fact that the "cubane" complex, $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$, (where acac refers to the monoanion of 2,4-pentanedione) studied by Bertrand, et al. (65) also exhibited a "normal" magnetic moment at both room temperature and liquid nitrogen temperature, is reason to suspect that the complex, Ni_2(DIIMINE)(OH), might possess a "cubane" structure, as indicated in (10). Since magnetic exchange effects in the "cubane", $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$, were not observed above 40°K, it would be interesting to study the low temperature magnetic behavior of the complex, Ni_2(DIIMINE)(OH), in order to provide further evidence to substantiate the claim that the structure is a "cubane" similar to (10).

To give added support to the formulations, Ni_2(DIIMINE)(OH) and



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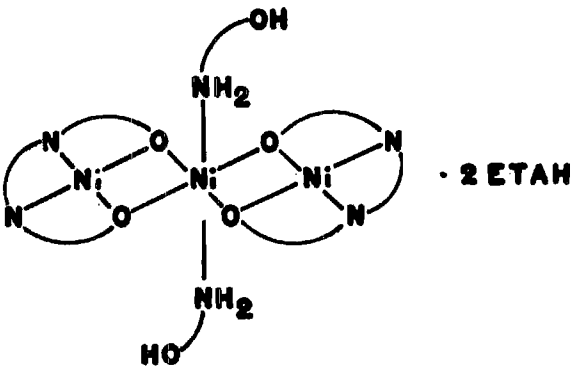
$Ni_3(DIIMINE)_2(ETAH)_4$, one should devise some means of detecting the presence of the DIIMINE chelate in these complexes. One such way in which any doubts as to the integrity of the diimine ligand can be dispelled is to locate the ligand absorption in the u.v. spectrum. Once the location of the u.v. absorption due to the conjugated six-membered chelate ring can be found in the u.v. spectra of the known DIIMINE containing complexes, one can simply look for that absorption in the u.v. spectra of the complexes tentatively formulated as $Ni_2(DIIMINE)(OH)$ and $Ni_3(DIIMINE)_2(ETAH)_4$. Spectral studies of this type are currently underway.

The complex, $Ni_3(DIIMINE)_2(ETAH)_4$, also has a magnetic moment that checks for one paramagnetic nickel ion per formula unit at both 298°K and 77°K. It may be possible to obtain suitably large single crystals of this compound, but none have yet been obtained. It seems unlikely that any other physico-chemical investigation, short of a complete x-ray structure determination, will reveal the true molecular structure of this complex. At least two structures for the complex are conceivable and both would agree with the observed magnetic moments. One is a complex salt of the formulation, $[Ni(DIIMINE)]_2[Ni(ETAH)_4]$, and the other is a trimer (11). In making both postulations, the guiding principle has been that there must be two diamagnetic nickel(II) ions and one paramagnetic nickel(II) ion per formula unit. Since square-planar nickel(II) complexes are invariably diamagnetic, and octahedral nickel(II) complexes are generally paramagnetic, both structures have been postulated to conform to these observations.

Future experimenters in this area of coordination chemistry might



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find it profitable to attempt preparations of the copper(II) analogs of the complexes, $Ni_3(DIIMINE)_2(ETAH)_4$ and $Ni_2(DIIMINE)(OH)$. These complexes, if they could be isolated, could provide further interesting examples of exchange coupled copper(II) clusters. In addition, the 1:2 diimine complexes of 2,4-pentanedione with 3-amino-1-propanol might prove to be structurally different from their 2-aminoethanol analogs and provide some interesting magnetic anomalies similar to that observed for the complexes, $[Cu(EIA)]_4$ and $[Cu(PIA)]_2$.

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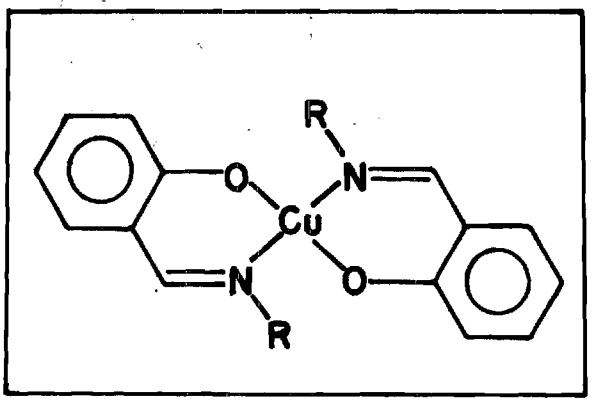
PART II

COMPLEXES WITH THE IMINE OF SALICYLALDEHYDE AND GLYCINE

CHAPTER I

INTRODUCTION

Salicylaldimine[1] complexes are among the oldest coordination compounds investigated by chemists. In fact, it has been over one-hundred years since Ettling first isolated the dark green crystalline complex known as bis(salicylaldimino)copper(II) (1, R=H). Since then, however, a huge number of publications have appeared, ranging from purely synthetic to modern physicochemical and biochemically relevant studies of these complexes. Because of the role that salicylaldimine complexes



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[1]Salicylaldimines are ligands formed from the condensation of a salicylaldehyde with an appropriate primary amine function.
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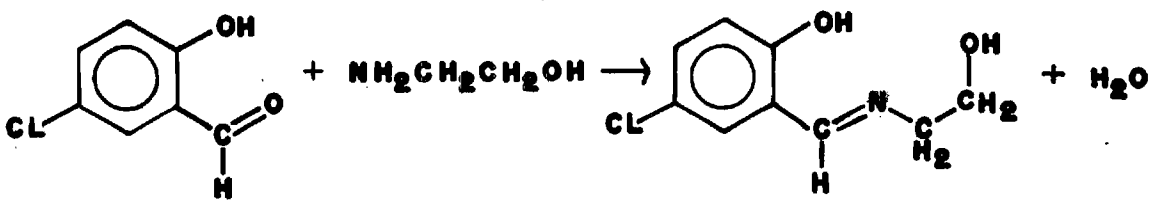
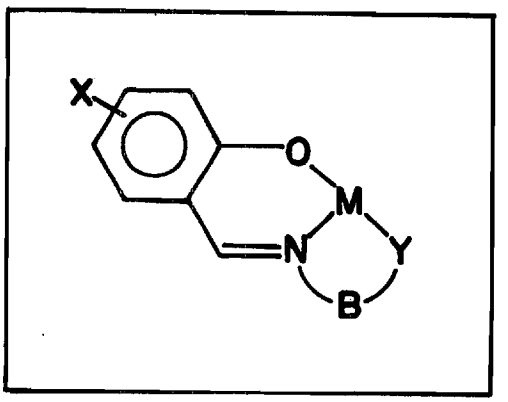


have occupied in the development of coordination chemistry, reviews have been written which cover both the historical significance of and current interests in salicylaldimine complexes (1,2).

One of many facets of interest in the salicylaldimine complexes has been the unusual kinds of magnetic behavior exhibited by some of them, especially those containing the potentially tridentate salicylaldimine ligands (2) (where Y is an atom or ion capable of coordinating to



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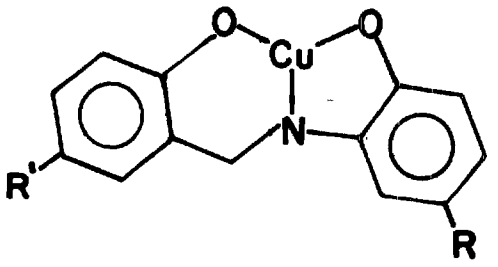
the metal, M, X is a ring substituent, and B is either an alkyl or aryl bridging group). Of course any understanding of these magnetically anomalous complexes presupposes a knowledge of their molecular structures. Consequently, crystal and molecular structure determinations generally accompany the magnetic studies in order to correlate structural features with magnetic behavior. Accordingly, this discussion will provide a brief review of the structural and magnetic studies that have been reported for the transition metal complexes containing potentially-tridentate salicylaldimine ligands.

Of all the potentially-tridentate salicylaldimine ligands, perhaps the most interesting are those with an oxygen atom as the third donor atom (2, Y=O). In fact, nearly all magnetically anomalous complexes pre-

pared to date have oxygen as the third donor atom of the ligand. For example, in the series of 5-substituted N-(2-hydroxyphenyl)-salicylideneimine complexes of copper(II) (3), Ginsberg (3) has measured the temperature dependence of the magnetic susceptibility between 1.4 and 300°K, and has shown that the magnetic behavior is characteristic of



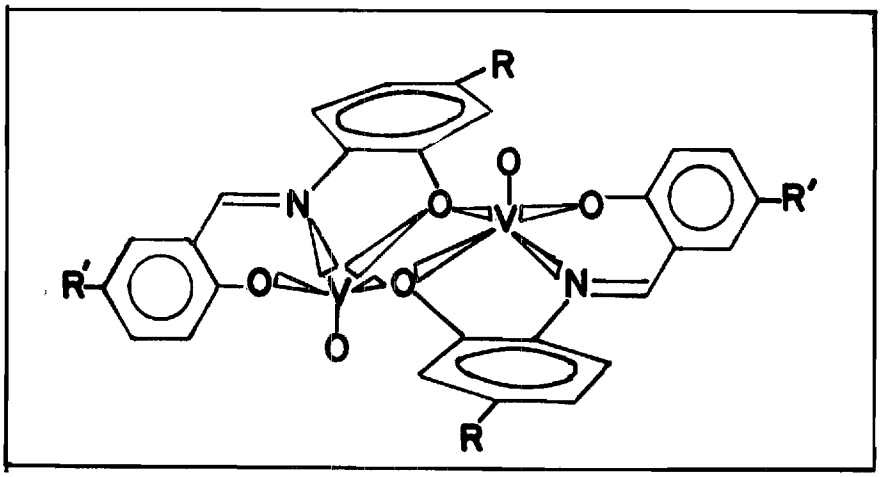
1. R=H; R′=H,CH_3,CL,BR
2. R=NO_2; R′=H,NO_2
3. R=CL; R′=H,CL

3

exchange-coupled antiferromagnetic pairs of copper ions. Since the magnetic susceptibilities of these complexes could be fit quite accurately to the Bleaney-Bowers equation (4) and since a closely related compound, acetylacetone-mono(o-hydroxyanil)copper(II), also has a susceptibility vs. temperature curve (5) which is closely reproduced by the Bleaney-Bowers equation, the molecular structures of the complexes in question were assumed to be identical. An x-ray structure determination (6) of the latter compound showed that the structure consisted of tetrameric units. Each tetrameric unit could be thought of as having been formed by displacing two phenolic-oxygen-bridged copper dimers (see Part I, 3). Hatfield (7) has demonstrated recently that the magnetic behavior of the acetylacetone-mono(o-hydroxyanil)copper(II) complex actually obeys the theoretical equation for the susceptibility of weakly bound tetrameric

units, and that minor deviations from the Bleaney-Bowers equation do occur in the temperature range, 96-400°K.

Ginsberg has also observed magnetic exchange in the analogous oxovanadium(IV) complexes of 5-substituted N-(2-hydroxyphenyl)-salicylideneimines (8). All but one of the complexes (R=H, R'=NO_2 ; 4) could be fit reasonably well to the Bleaney-Bowers equation for exchange coupled dimers. Unfortunately, no x-ray structures have been done to date which would confirm an oxygen-bridged dimeric structure (4) for these complexes. There is increasing interest in oxovanadium complexes of



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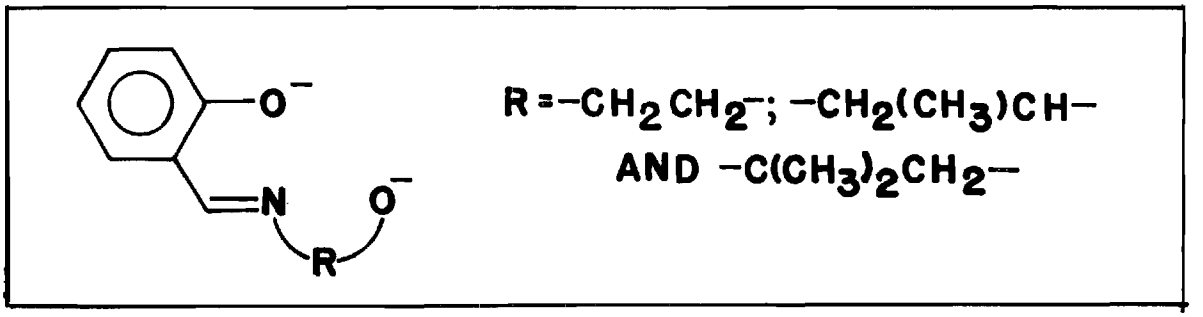
this type because of the possibility of additional weak intermolecular magnetic interactions through vanadium-vanadyloxygen-vanadium bridges (V→O=V). Such vanadyl bridges have been postulated as an explanation for the anomalous magnetic behavior of the oxovanadium(IV) complex in (4) with R=H and R'=NO_2. In addition, the existence of bridging vanadyl groups in the solid state have been confirmed by a recent x-ray structure determination (9) of the complex, N,N'-propylenebis(salicylal-

diminato)oxovanadium(IV). Although a temperature dependent magnetic susceptibility study (10) on this compound in the temperature range 95-295°K did not show any appreciable deviation from Curie-Weiss dependence ($\mu_{eff}^{295°K}$ = 1.78 B. M., θ = -7°K), it does not exclude the possibility of appreciable magnetic interactions at temperatures below 95°K.

The fact that significant magnetic interactions might be observable only at very low temperatures is exemplified quite well by the copper(II) complexes with the dianion of N-(hydroxyalkyl)salicylideneimines (5). All of the complexes have normal magnetic moments (1.87 B. M.) at room temperature, and have linear susceptibility curves (χ vs. 1/T) in the temperature range 80-300°K, characteristic of Curie-Weiss



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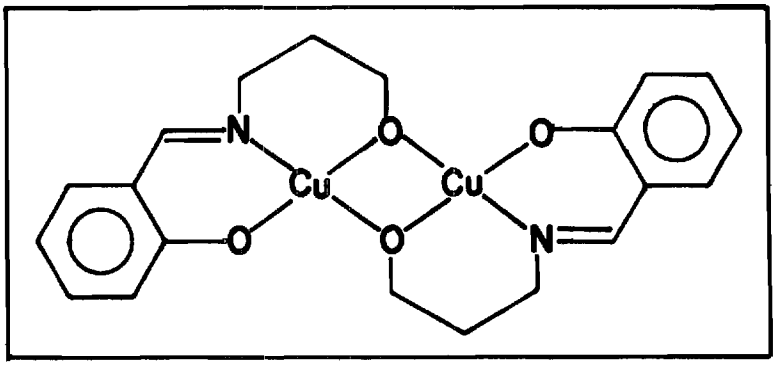
law behavior (11). Nevertheless, Kishita et al. (12) have reported that the complex, Cu(SALETA), (where SALETA is ligand 5 with R=CH_2CH_2 is tetrameric in benzene solution and exhibits a complex temperature dependent magnetism identical to that of the tetramer, $[Cu(EIA)]_4$, (see Part I, 4; where EIA represents the dianion of the tridentate monoimine of 2,4-pentanedione and 2-aminoethanol). On the basis of this information, Tokii,

et al. (11) have attributed the same type of tetrameric structure to other copper(II) complexes with the dianions of N-hydroxyalkylsalicylideneimines (ligand 5 with R= $-CH_2(CH_3)CH-$ and $-C(CH_3)_2CH_2-$).

On the other hand, Tokii, et al. also point out that for the copper(II) complex with the dianion of N-(3-hydroxypropyl)salicylideneimine, Cu(SALPA), (where SALPA is the ligand in 5 with R= $-CH_2CH_2CH_2-$) the overwhelming evidence points to an oxygen-bridged dimeric structure (6). First of all, the complex has a low room temperature magnetic moment of 0.43 B.M. and secondly, the magnetic behavior conforms to the Bleaney-bowers equation for a bridged binuclear structure. Finally, the complex is closely related to the copper(II) complex with the Schiff base[2] of 2,4-pentanedione and 3-amino-1-propanol, $[Cu(PIA)]_2$, (see Part I, p. 5; where PIA represents the dianion of the monoimine of 2,4-pentanedione and 3-amino-1-propanol) which also has a low room temperature magnetic moment of 0.41 B.M. (13). In addition, the x-ray structure determination



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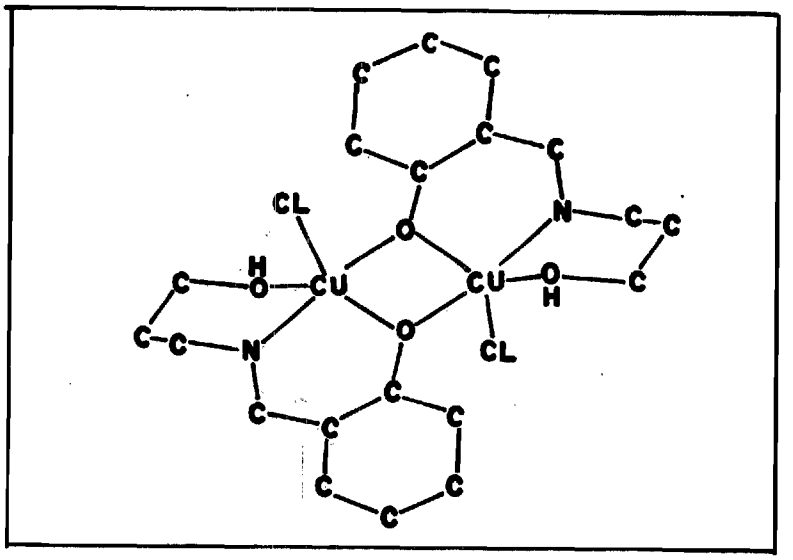
(14) of the complex, Cu(SALPAH)Cl, (where SALPAH represents the monoan-

[2]A Schiff base is a compound which can be made by reacting aldehydes or ketones with primary amines, resulting in the formation of the azomethine group, >C=N-R. The Schiff base so formed can then coordinate to metals through the electron pair on the nitrogen atom.

ion of the tridentate Schiff's base of salicylaldehyde and 3-hydroxy-1-propanol) also revealed a dinuclear structure, but the copper ions in that structure are bridged by phenolic oxygens rather than alcoholic oxygens (7). The coordination of copper is approximately trigonal-bipyramidal and the complex has a subnormal room temperature magnetic moment of 1.05 B.M.



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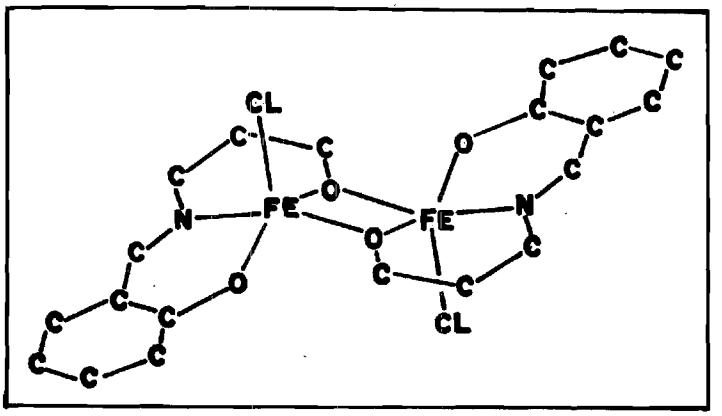
Other metal ions also form oxygen-bridged binuclear complexes with the dianion of N-3-hydroxypropylsalicylideneimine. The reaction of ferric chloride with the preformed ligand in alkaline methanol solution results in a dark brown crystalline product, Fe(SALPA)Cl, which can be recrystallized from tetrahydrofuran. Recrystallization of the complex from toluene produced crystals with the formulation Fe(SALPA)Cl·$\frac{1}{2}$Toluene. Single crystal x-ray diffraction studies by Breece (15) and magnetic studies by Baker (26) have confirmed the dimeric structure (8) in both crystals. The iron atom has tetragonal-pyramidal coordination and is displaced 0.55Å from the basal plane of the O_3N donor atoms. The mag-

netism of the complex could be fit to the Van Vleck expression for antiferromagnetic exchange-coupled ($J = -17\ cm^{-1}$) iron(III) ions of a dimer.



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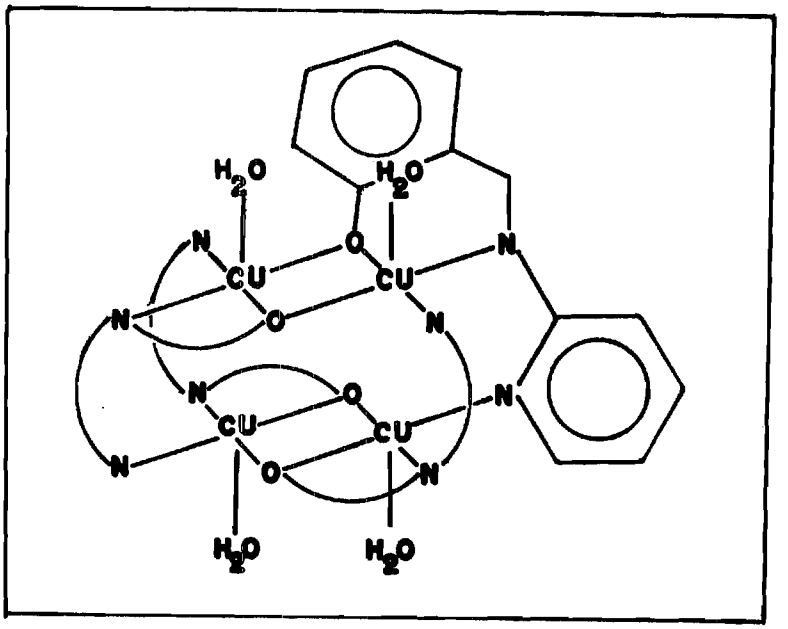
There is some evidence (15) that complexes of cobalt(II) and nickel(II) with the dianion of N-(3-hydroxypropyl)salicylideneimine, $(SALPA)^{2-}$, contain polynuclear units. With cobalt(II), a complex of the formulation, $Co(SALPA)\cdot\frac{1}{2}H_2O$, is formed and the magnetic moment ($\mu_{eff}^{298^\circ K} = 4.41$ B.M.) is consistent with that expected for cobalt(II) (4.1-5.2 B.M. (17)). Since there is a 1:1 ligand-to-metal ion ratio, it is quite possible that the complex is associated into polynuclear units similar to $[Cu(EIA)]_4$. It should also be pointed out that an analogous cobalt(II) complex, Co(EIA), was found to be isomorphous with $[Cu(EIA)]_4$, and hence must be tetrameric (18), (i.e. $[Co(EIA)]_4$).

With nickel(II) ions, complexes with the formulation, Ni(SALPA)·Ethanol and Ni(SALPA), are formed and are presumed analogous to the complexes, Ni(EIA)·Methanol and Ni(EIA), respectively. The structure of Ni(EIA) (19) consists of oxygen-bridged binuclear units containing diamagnetic nickel(II) ions with square-planar coordination. The dimer is not entirely planar, however, but is bent along an imaginary line con-

necting the two bridging oxygen atoms; this results in a dihedral angle of 38.8°. Since the corresponding complex, Ni(SALPA), has a similar red color, the same metal to ligand ratio, and also gives a green alcoholate complex, Ni(SALPA)·Ethanol, a dimeric structure is assumed. The structure of the green alcoholates, Ni(SALPA)·Ethanol and Ni(EIA)·Methanol are assumed to be similar and presumably contain polynuclear units. They have properties (18) similar to the complex, $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]$, which has a tetrameric structure (20).

A rather novel tetrameric structure is found for the complex, N-(2-pyridyl)salicylaldiminatoaquocopper(II) nitrate. The structure (21) is novel because the tetramer can be thought of as having been formed by stacking two dimeric units atop one another with the tridentate ligands holding the dimers together (9). Other tetrameric units encountered previously have had bridging oxygen atoms shared between three



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different metal ions. For the complex, $[Cu(EIA)]_4$, the result was a

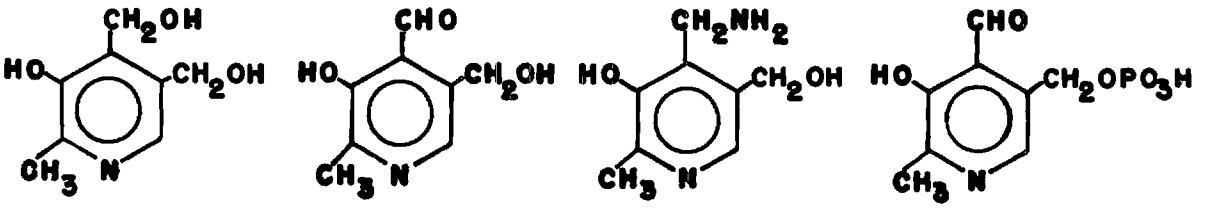
"cubane-like" unit (see Part I, 4), while for the complex, acetylacetone-mono-(o-hydroxyanil)copper(II), the result was a tetramer of "displaced dimers" (see Part I, 3). Both of these tetrameric complexes exhibited rather complex magnetic behavior because each copper ion is spin-coupled to more than one magnetically nonequivalent copper ion. On the other hand, the magnetic susceptibility of the tetranuclear complex, tetrakis-[N-(2-pyridyl)salicylaldiminatoaquocopper(II)]tetranitrate, (9), over the temperature range, 90-300°K, indicated antiferromagnetic coupling between oxygen-bridged copper ions only ($J = -41$ cm^{-1}). Consequently, the tetramer can be treated as essentially two independent binuclear units since the interactions between dimers are either very weak or non-existent.

The chemist's interest in tetrameric and/or polynuclear metal ion clusters actually extends beyond an interest in their unusual magnetic properties. In recent years, considerable attention has been paid to the role that metal ions play in catalyzing certain biological processes. A number of metalloenzymes have been found to contain several metal ions per molecule (e.g. ferrodoxin (22) and cerruloplasm (23)). Since the properties associated with the metal ions in these compounds are often different from those observed for mononuclear complexes, the preparation of new polynuclear complexes, which serve as models for the physical and chemical properties of metalloenzymes, is receiving considerable attention.

It is also known that metal ions are important cofactors in non-enzymatic systems that model the catalytic activity of vitamin B_6 towards certain reactions of amino acids (24), such as transamination

(25-28), racemization (29), and oxidative deamination (30,31; see below). Although "vitamin B_6" actually refers to a group of very closely related compounds (32,33) (namely, pyridoxol (I), pyridoxal (II), pyridoxamine (III), and pyridoxal phosphate (IV)--see structures I-IV below), certain substituted salicylaldehyde derivatives (especially 4-and 6-nitrosalicylaldehyde) are known to be effective replacements for vitamin B_6 (i.e. pyridoxal) in the oxidative deamination of amino acids. In addition, the work of Metzler and Snell (24) demonstrated that an important prerequisite for the catalytic activity of pyridoxal in model systems is the formation of Schiff base chelates with transition metal ions. Pursuant

EXAMPLE OF A PYRIDOXAL CATALYZED OXIDATIVE DEAMINATION REACTION



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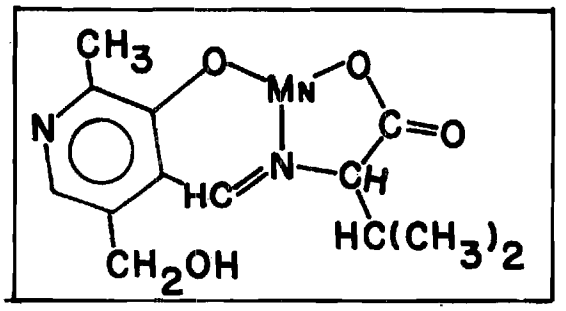
to these observations, numerous experimenters have attempted to isolate the Schiff base complexes responsible for the catalytic activity, in order to understand the mechanisms involved in the model reactions. Since there are obvious structural similarities between the Schiff bases of pyridoxal and salicylaldehyde, inferences concerning the structures of the catalytically active Schiff base complexes are often made from

known structures of pyridoxal or salicylaldehyde Schiff base complexes. In recent years, three structures have been reported that involve coordinated Schiff bases of pyridoxal with amino acids (34-36). Hoard has published (34) the structure of a manganese(II) complex containing the monovalent Schiff base of pyridoxal and d,l valine, $Mn(PyrVal)_2 \cdot 2H_2O$. Figure (10) shows one of the coordinated ligands about the manganese.



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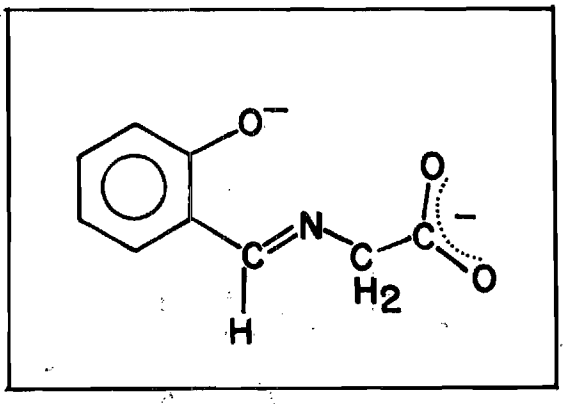
The coordinated atoms (2 oxygens and 1 nitrogen) of one ligand are in a plane with the manganese atom, and this plane is perpendicular to the corresponding plane of the other ligand; the coordination about manganese is octahedral. This arrangement could allow for essential planarity of the fused-ring system in the catalytic reactions. A twofold-axis bisecting a specific opposite pair of octahedral edges renders the two $(PyrVal)^{2-}$ chelates structurally equivalent. There is a dihedral angle of roughly 150° between the mean planes of the pyridoxylidene and valinate rings. The entire molecular framework is stabilized by extensive intermolecular hydrogen bonding involving a carboxylate oxygen and a pyridine nitrogen (2.68Å); another carboxylate oxygen with a water molecule (2.69Å); and the same water molecule with the hydroxymethyl oxygens of two different complexes (2.65 and 2.74Å).

Two other structures have been reported by Waters et al. (35,36). They are the structures of (±)-phenylalanine-(pyridoxylidene-5-phosphate) copper(II) and (±)-valine-pyridoxylidene copper(II). Both structures involved five-coordinated tetragonal-pyramidal copper and, since the metal to ligand ratio in these complexes is 1:1, the two additional coordination positions about copper are filled by donor atoms from adjacent molecules. In the former complex, these atoms are a water oxygen and a phosphate oxygen, while in the latter complex, they are a pyridoxyl nitrogen and a hydroxymethyl oxygen. The coordination of the Schiff base ligand in both complexes could allow for essential planarity of the chelate rings as a whole (excluding side chains). Some twisting away from coplanarity of the fused ring system was observed, and was believed to be the result of packing forces in the crystal. The importance that the authors place upon these three structures is that they support Metzler's explanation (24) of the primary function of the metal ion in all the metal catalyzed reactions of vitamin B_6 with amino acids; namely, that the coordination of a Schiff base ligand in the transition metal ion intermediate allows for essential planarity of the fused-ring system, thereby facilitating electron displacements that lead to transamination, racemization or oxidative deamination.

Because of this general interest in Schiff base complexes of pyridoxal with amino acids, other workers have reported the preparation of complexes containing the structurally similar Schiff bases of salicylaldehyde with amino acids. Theriot (37) has isolated several oxovanadium(IV) complexes of the formulation, [VO(SALAMINO)(H_2O)], (where

SALAMINO represents the dianion of a Schiff base of salicylaldehyde with an amino acid) which is believed to be oxygen-bridged and dinuclear. The complexes have room temperature magnetic moments in the range, 0.49-0.78 B.M. Theriot (38) has also isolated nickel(II) complexes of the formulation, $Ni(SALAMINO)(H_2O)_2$. The electronic spectra and molecular weight data support a dinuclear structure. On the other hand, the magnetic moments range from 3.10 to 3.40 B.M. and are typical of high-spin nickel(II) in octahedral, trigonal-bipyramidal and tetragonal-pyramidal fields. Theriot postulates an oxygen-bridged dinuclear structure for these complexes even though the magnetic data do not give any indication of significant antiferromagnetic interactions.

Another series of Schiff base complexes of salicylaldehyde and amino acids was reported some time ago by Ray and Mukherjee (39,40). Of particular interest were the cobalt, iron and manganese complexes that contained the divalent Schiff base of salicylaldehyde and glycine, $(SALGLY)^{2-}$, (11). For cobalt(II), Ray and Mukherjee reported a compound



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of the formulation, $Co(SALGLY)(GLYCINE)\cdot\frac{1}{2}H_2O$, having a room temperature magnetic moment ($\mu_{eff}^{298^\circ K}$ = 2.89 B.M.) that is considerably low for cobalt(II), a d^7 metal ion. With iron(III), a complex of the formula-

tion, $Fe_2(SALGLY)_2(GLYCINATE)(OH)$, was purported to have a magnetic moment of 5.91 B.M. The manganese(II) complex was formulated as Mn(SALGLY)(GLYCINE), with a magnetic moment of 5.84 B.M. The authors further contended that the composition of the manganese complex resembled that of the copper complex, Cu(SALGLY)(GLYCINE).

Since these compounds were reported, the x-ray structures of three copper(II) complexes containing Schiff base ligands of salicylaldehyde and amino acids have appeared in the literature; namely, N-salicylideneglycinatoaquocopper(II)-hemihydrate (41) $[Cu(SALGLY)(H_2O)]\cdot\frac{1}{2}H_2O$, tetrahydrate (42) $[Cu(SALGLY)(H_2O)]\cdot 4H_2O$, and N-salicylidene-α-aminoisobutyratoaquocopper(II) (43) [Cu(SAL-i-BUT)(H_2O)]. Interestingly enough, all three of these structures involve tetragonal-pyramidal coordination of the copper ion, and, in accordance with Metzler's hypothesis (24), all show little or no distortions from overall planarity of the dianion of the tridentate Schiff base. It is also interesting that, in all cases, an aquo ligand rather than an amino acid ligand occupies a position in the tetragonal-pyramidal coordination of the copper ion. This observation is in sharp contrast to the proposed structure and composition of the salicylideneglycinate copper complex, Cu(SALGLY)(GLYCINE), reported by Ray and Mukherjee.

Because of the dissimilarity in Ray and Mukherjee's formulation of the copper salicylideneglycinate complex with the formulations reported by other authors for similar complexes of copper, it raises some doubts as to the correctness of Ray and Mukherjee's formulations for the salicylideneglycinate complexes of cobalt, iron and manganese. In order to expose the true formulations of these complexes and to explain the

low magnetic moment observed for the cobalt salicylideneglycinate complex, this thesis will report the results obtained from analytical, magnetic susceptibility, and single-crystal x-ray diffraction studies on these complexes.

CHAPTER II

EXPERIMENTAL

Preparation of Complexes[1]

Cobalt Complex of the Dianion of the Schiff's Base of Salicylaldehyde and Glycine, $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$

The preparation of this complex was performed following the directions given by Ray and Mukherjee (39). To 4.0 grams (0.053 moles) of glycine dissolved in water (50 ml.) was added 3.0 grams (0.010 moles) of bis(salicylaldehydato)cobalt(II). The mixture was shaken and heated on a water bath until all the reactants had dissolved. The mixture was then filtered while hot and the filtrate set aside for crystallization. After standing for several hours, violet-brown needles formed from the solution. The crystals were washed first with water, then with alcohol, and finally, dried in air. The crystals were suitable for x-ray diffraction studies.

Anal. Calcd. for $Co_3C_{36}H_{44}N_4O_{20}$: C, 41.99; H, 4.31; N, 5.44

Found: C, 42.54; H, 4.33; N, 5.38

Iron Complex of the Dianion of the Schiff's Base of Salicylaldehyde and Glycine, $[Fe(H_2O)_6][Fe(SALGLY)_2]_2 \cdot 2H_2O$

According to the method published by Ray and Mukherjee (39), 1.5 grams (0.0055 moles) of ferrous sulfate heptahydrate, dissolved in a little water (50 ml.), was treated with 0.62 grams (0.0083 moles) of

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[1]Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

glycine followed by the addition of an alcoholic solution (25 ml.) containing 0.61 grams (0.0055 moles) of salicylaldehyde. The deep red solution was refluxed on a water bath for about two hours, after which dark red shining crystals gradually separated from the cooling solution. The crystals were filtered off, washed with water and alcohol, and finally dried in air. Crystals suitable for x-ray work were obtained in this manner.

Anal. Calcd. for $Fe_3C_{36}H_{44}N_4O_{20}$: C, 42.39; H, 4.31; N, 5.49
Found: C, 42.26; H, 4.40; N, 5.32

Manganese Complex of the Dianion of the Schiff's Base of Salicylaldehyde and Glycine, $[Mn(H_2O)_6][Mn(SALGLY)_2]_2 \cdot 2H_2O$

To a flask containing 3.0 grams (0.015 moles) of manganese(II) chloride tetrahydrate dissolved in water (100 ml.) was added 4.0 grams (0.033 moles) of salicylaldehyde, 5.0 grams (0.036 moles) of sodium acetate and 2.5 grams (0.033 moles) of glycine. The mixture was stirred and set aside without stoppering the flask. After several days, the dark violet-brown needle crystals, which formed on the surface of the mother liquor, were collected by filtration, washed with water and alcohol, and finally dried in air. The crystals were adaptable to study by x-ray diffraction techniques.

Anal. Calcd. for $Mn_3C_{36}H_{44}N_4O_{20}$: C, 42.48; H, 4.36; N, 5.50
Found: C, 42.06; H, 4.23; N, 5.08

Sodium Salt of the Manganese(II) Complex Anion of Salicylaldehyde and Glycine, $Na_2[Mn(SALGLY)_2] \cdot 3H_2O$

To a flask containing an aqueous solution (50 ml.) of 1.6 grams (0.040 moles) of sodium hydroxide and 1.5 grams (0.020 moles) of glycine was added an ethanolic solution (50 ml.) of 2.4 grams (0.020 moles) of

salicylaldehyde. To the resultant mixture, an aqueous solution (50 ml.) of 2.0 grams (0.010 moles) of manganese(II) chloride tetrahydrate was added dropwise. The mixture was stirred and filtered cold. The filtrate was heated on the water bath, whereupon light yellow-colored crystals formed from the hot solution. The crystals, which were collected by filtration, were susceptible to slow discoloration when wet. An x-ray structure determination of the complex could not be done because the crystals were too small and they could not be grown larger due to decomposition of the solution.

Anal. Calcd. for $Na_2MnC_{18}H_{20}N_2O_9$: C, 42.45; H, 3.96; N, 5.50
Found: C, 42.82; H, 3.78; N, 5.40

Magnetic Studies

All magnetic susceptibility measurements were made by the Faraday method in the manner outlined in Part I of this thesis. The magnetic data compiled for the cobalt complex, $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$, are presented in Table 1.

Table 1. Magnetic Data for $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$ at 294.7°K

Current J	Susceptibility per Gram of Complex $\chi_g \times 10^5$	Susceptibility per Formula Unit $\chi_m \times 10^5$	Magnetic Moment per Formula Unit $\mu_{eff}^{294.7°K}$; B.M.
4	1.036	1124.	5.169
5	1.034	1122.	5.166
6	1.036	1124.	5.169
7	1.038	1126.	5.174
8	1.023	1110.	5.138
9	1.022	1110.	5.138

Table 1. (Continued)

Current	Susceptibility per Gram of Complex	Susceptibility per Formula Unit	Magnetic Moment per Formula Unit
J	$\chi_g \times 10^5$	$\chi_m \times 10^5$	$\mu_{eff}^{294.7^\circ K}$; B.M.
10	1.025	1113.	5.143

Average $\mu_{eff}^{294.7^\circ K} = 5.15(2)$ B.M.

EQUIV = 1029.43 $g\text{-}m^{-1}$; formula weight

DIAMAG = 577.36×10^{-6} m^{-1}; calculated for one formula unit

FORMULA UNIT = $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$

Crystallographic Studies

Calculations

Computations were performed on both a Burroughs 5500 computer and a Univac 1108 computer. All programs used have been mentioned previously in Part I of this work.

Solution of the Structure of $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$

A violet-brown needle crystal of approximate dimensions 0.10 x 0.15 x 0.85 mm. was mounted on a glass fiber with the long dimension of the crystal parallel to the fiber. Precession photographs indicated an orthorhombic crystal system. The space group Pbcn was identified by the systematic absences: $hk0$, $h+k = 2n+1$; $0kl$, $k = 2n+1$; and $h0l$, $l = 2n+1$.

The crystal was transferred to an automatic Picker four-angle diffractometer; unit cell parameters were obtained by a least-squares

refinement of 16 manually-centered reflections. The cell parameters obtained were: $a = 9.535(7)$Å, $b = 12.249(9)$Å, $c = 37.028(33)$Å, $\alpha = \beta = \gamma = 90^\circ$ and $V = 4325$Å^3 (25°C, molybdenum radiation, $\lambda = 0.7107$Å). The calculated density of 1.58 g-cm^{-3}, based on four formula units per unit cell, agreed exactly with the observed density of 1.58(1) g-cm^{-3}, measured by the flotation method using a mixture of chloroform and methylene iodide.

The manner in which the intensity measurements were made and later corrected for background, Lorentz, and polarization effects have been described in Part I of this work. Of a total of 5720 reflections collected, only 1867 were accepted as statistically above background ($\sigma(I)/I < 0.30$; $p = 0.00$). Since the calculated value for the linear absorption coefficient ($\mu = 12.71$ cm^{-1}) was not considered large enough to significantly affect the data, the intensities were not corrected for absorption. The intensity of a standard reflection (2,1,12) was monitored at intervals of 50 reflections and showed no significant variation during data collection.

A three-dimensional Patterson function was calculated using all 1867 unique nonzero reflections. From an inspection of the most intense peaks appearing on the Harker lines $(0,2y,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}+2z$; $\frac{1}{2}+2x,\frac{1}{2},0)$ in the Patterson map, the positions for a complete eight-fold set of cobalt atoms were obtained. Further inspection of the Patterson map did not reveal a second eight-fold set of cobalt atoms, consistent with the fact that prior chemical analysis supported a trinuclear formulation for the compound. This suggested that the remaining set of cobalt atoms of the trimer occupy special four-fold positions in the lattice. For the space

group, Pbcn, there are two kinds of special positions; namely, a fourfold set of positions coincident with twofold rotation axes, and two fourfold sets of positions coincident with centers of inversion. In order to determine which set of special positions to use, the cobalt atoms of the special positions were assumed to lie along the shortest internuclear vector between cobalt atoms of the eightfold set. The correct choice of special positions was made by determining which symmetry element related the cobalt atoms at the termini of the shortest internuclear vector. The Patterson map indicated that the two cobalt atoms of the eightfold set having the shortest internuclear vector between them corresponded to cobalt atoms that were related by twofold rotation axes. Consequently, the second set of cobalt positions was determined to be the fourfold special set coincident with the twofold rotation axes in Pbcn.

An electron density calculation, phased on the coordinates of the cobalt atoms, revealed the positions of all the remaining non-hydrogen atoms. Least-squares refinements of the scale factor, coordinates and isotropic temperature factors were carried out using the weighting scheme mentioned previously. Since a subsequent electron density map showed considerable anisotropic thermal motion for the cobalt ions, anisotropic thermal parameters were employed for the cobalt ions. The hydrogen atoms were either located from electron density maps or placed in calculated positions. The residuals, R_1 and R_2, from the last cycle of full-matrix least-squares refinement were 0.098 and 0.056 respectively. Table 2 lists the final positional and thermal parameters for all the atoms of the structure, while Table 3 lists the observed and calculated structure factors for all 1867 unique nonzero reflections.

Table 2. Final Positional and Thermal Parameters for $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$

Atom	x	y	z	B^a, Å^2
Co1	0.0380(2)	0.0398(2)	0.13731(6)	1.56(3)[b]
Co2	$\frac{1}{2}$	0.0251(2)	$\frac{1}{4}$	1.91(6)[c]
OW1	0.357(1)	-0.0988(7)	0.2582(3)	2.5(2)
OW2	0.4290(9)	0.0263(9)	0.1952(2)	3.5(2)
OW3	0.351(1)	0.1350(8)	0.2640(2)	2.9(2)
OW4	0.618(1)	0.0153(8)	0.1433(3)	4.7(3)
HW1a	0.32	-0.16	0.24	-
HW1b	0.30	-0.115	0.277	-
HW2a	0.347	0.032	0.185	-
HW2b	0.48	0.02	0.18	-
HW3a	0.34	0.18	0.28	-
HW3b	0.283	0.134	0.248	-
HW4a	0.62	0.09	0.14	-
HW4b	0.59	-0.04	0.123	-
LIGAND 1				
C1	0.268(1)	0.061(1)	0.0905(4)	2.2(3)
C2	0.346(1)	0.124(1)	0.0666(4)	2.6(3)
C3	0.456(2)	0.078(1)	0.0491(6)	5.7(5)
C4	0.486(2)	-0.026(1)	0.0495(5)	5.3(4)
C5	0.411(1)	-0.097(1)	0.0744(5)	3.3(4)
C6	0.300(1)	-0.053(1)	0.0934(4)	1.8(3)
C7	0.245(1)	-0.123(1)	0.1202(4)	2.5(3)
C8	0.065(1)	-0.172(1)	0.1638(4)	3.1(4)
C9	-0.077(1)	-0.130(1)	0.1770(4)	2.2(3)
O1	0.175(1)	0.1108(8)	0.1104(2)	1.9(2)
O2	-0.1052(9)	-0.0294(9)	0.1673(2)	2.2(2)
O3	-0.149(1)	-0.1830(7)	0.1968(3)	3.1(2)
N1	0.133(1)	-0.0992(8)	0.1363(3)	1.3(2)

Table 2. (Continued)

Atom	x	y	z	B^a, Å^2
HC2	0.295	0.163	0.053	-
HC3	0.47	0.12	0.023	-
HC4	0.54	-0.06	0.035	-
HC5	0.44	-0.18	0.076	-
HC7	0.24	-0.19	0.11	-
HC8a	0.03	-0.23	0.145	-
HC8b	0.12	-0.22	0.177	-
LIGAND 2				
C1	-0.111(1)	0.072(1)	0.0717(4)	2.4(4)
C2	-0.121(1)	0.034(1)	0.0375(4)	3.7(4)
C3	-0.178(2)	0.106(1)	0.0127(5)	4.9(5)
C4	-0.237(2)	0.212(1)	0.0217(4)	4.6(4)
C5	-0.221(1)	0.239(1)	0.0571(5)	3.2(4)
C6	-0.150(1)	0.178(1)	0.0825(4)	2.2(3)
C7	-0.126(1)	0.215(1)	0.1178(4)	1.8(3)
C8	-0.036(1)	0.222(1)	0.1785(4)	2.4(3)
C9	0.099(1)	0.174(1)	0.1952(5)	2.2(3)
O1	-0.0557(9)	0.0010(7)	0.0940(2)	2.3(2)
O2	0.1370(9)	0.0825(7)	0.1815(2)	1.5(2)
O3	0.147(1)	0.2140(9)	0.2225(3)	4.0(3)
N1	-0.057(1)	0.1762(8)	0.1433(3)	1.9(2)
HC2	-0.26	0.30	0.07	-
HC3	-0.25	0.253	0.00	-
HC4	-0.18	0.066	-0.015	-
HC5	-0.09	-0.04	0.03	-
HC7	-0.16	0.30	0.12	-
HC8a	-0.110	0.178	0.193	-
HC8b	-0.04	0.30	0.18	-

Table 2. (Continued)

[a]Final isotropic value obtained before converting to anisotropic temperature factors expressed as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

[b]The anisotropic temperature factors ($\times 10^4$) for Co1 refined as follows: $\beta_{11} = 44(2)$, $\beta_{22} = 19(1)$, $\beta_{33} = 3.8(2)$, $\beta_{12} = 4(2)$, $\beta_{13} = 3.0(7)$ and $\beta_{23} = 0.2(6)$

[c]The anisotropic temperature factors ($\times 10^4$) for Co2 refined as follows: $\beta_{11} = 48(3)$, $\beta_{22} = 23(2)$, $\beta_{33} = 4.7(3)$, $\beta_{13} = 0.8(8)$. The values for β_{12} and β_{23} are zero by symmetry.

Table 3. Observed and Calculated Structure Factors for $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
	L= 0			7	2	50	57	3	10	58	50	1	6	112	104
				2	3	52	46	4	10	56	57	3	6	52	54
2	0	247	244	4	3	49	43	6	10	78	71	4	6	38	39
4	0	138	128	6	3	69	71	7	10	34	38	5	6	36	39
6	0	67	71	9	3	41	42	1	11	30	34	1	7	81	80
8	0	47	53	11	3	36	22	2	12	35	48	4	7	50	41
1	1	167	160	13	3	35	28	4	12	57	52	5	7	31	26
3	1	49	46	0	4	118	116	1	13	32	32	7	7	33	31
5	1	98	95	1	4	52	51	1	15	32	35	3	8	47	41
7	1	52	46	2	4	134	131	1	17	46	47	5	8	79	76
9	1	77	79	3	4	55	51					1	9	41	34
11	1	77	73	4	4	122	117		L= 2			4	9	105	104
13	1	52	62	5	4	125	116					6	9	47	55
2	2	349	350	6	4	40	36	1	0	87	91	2	10	28	24
4	2	83	88	7	4	70	61	2	0	213	207	3	10	36	38
1	3	145	149	9	4	46	49	3	0	27	41	5	10	79	81
3	3	78	58	1	5	83	80	4	0	117	109	7	10	55	57
7	3	30	31	2	5	42	35	5	0	132	120	4	11	64	69
9	3	48	48	3	5	29	24	6	0	80	87	6	11	70	73
11	3	42	47	4	5	57	55	7	0	117	118	8	11	45	52
13	3	50	47	6	5	73	59	8	0	51	51	2	12	31	32
0	4	110	111	8	5	49	60	9	0	55	54	5	12	66	68
2	4	255	256	9	5	57	57	1	1	51	60	7	12	56	67
4	4	191	178	11	5	57	59	5	1	59	51	4	13	50	49
12	4	32	27	0	6	252	252	6	1	47	44	6	13	58	65
1	5	134	120	2	6	189	182	7	1	65	60	8	13	35	38
5	5	57	52	3	6	38	43	8	1	106	108	2	14	36	30
7	5	33	36	4	6	94	95	10	1	64	47	3	14	41	50
9	5	54	45	5	6	93	86	11	1	34	26	5	14	35	44
11	5	48	50	9	6	34	32	1	2	130	132	7	14	33	39
0	6	41	54	2	7	41	34	4	2	105	104				
2	6	167	154	3	7	64	56	5	2	118	115		L= 3		
4	6	41	37	4	7	43	32	7	2	133	122				
12	6	34	21	6	7	50	50	8	2	41	43	1	1	103	102
1	7	82	100	7	7	53	46	9	2	70	72	2	1	109	110
3	7	41	46	8	7	34	36	1	3	174	171	3	1	25	25
7	7	95	87	9	7	51	45	2	3	29	37	4	1	90	83
2	8	42	28	10	7	44	40	3	3	77	74	5	1	29	28
1	9	71	74	11	7	50	46	4	3	58	56	0	2	124	112
3	9	60	62	0	8	115	128	6	3	52	50	1	2	122	114
5	9	37	31	1	8	33	34	8	3	92	82	2	2	22	17
2	10	55	57	2	8	133	132	10	3	32	35	3	2	64	65
4	10	101	87	3	8	51	47	0	4	23	26	4	2	44	36
1	11	43	40	4	8	89	80	1	4	165	157	6	2	27	26
3	11	91	80	5	8	59	61	2	4	114	115	7	2	33	30
0	12	87	91	1	9	56	66	4	4	68	61	10	2	43	34
				2	9	44	38	5	4	85	79	1	3	140	135
	L= 1			3	9	37	39	6	4	44	42	2	3	176	166
				4	9	61	51	7	4	80	68	3	3	95	92
1	1	98	105	6	9	44	36	10	4	34	29	4	3	92	88
2	1	95	92	7	9	36	42	2	5	105	88	5	3	43	43
0	2	180	183	8	9	39	28	3	5	115	108	6	3	57	56
1	2	65	58	9	9	38	38	4	5	65	46	8	3	63	60
2	2	85	83	11	9	37	33	6	5	38	32	1	4	68	62
3	2	24	18	0	10	90	103	9	5	31	28	3	4	166	156
6	2	62	58	2	10	66	77	0	6	128	120	5	4	116	109

Table 3. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
6	4	36	32	8	12	40	31	6	6	34	41	9	4	33	30
7	4	75	74	3	13	31	36	8	6	54	39	10	4	51	59
9	4	38	38	0	14	37	33	2	7	67	58	1	5	112	112
10	4	40	33	2	14	38	40	5	7	46	46	2	5	72	66
12	4	32	24	0	16	36	39	0	8	61	65	3	5	205	203
1	5	140	136					1	8	24	20	4	5	59	52
2	5	90	76		L=	4		2	8	47	50	5	5	95	87
3	5	131	121					3	8	58	55	6	5	58	53
4	5	93	86	0	0	312	281	4	8	34	33	8	5	34	33
5	5	60	58	1	0	33	21	5	8	34	31	0	6	89	97
6	5	68	68	2	0	127	128	6	8	32	22	1	6	70	64
8	5	33	45	3	0	46	55	1	9	29	32	2	6	90	83
9	5	33	30	6	0	109	111	3	9	71	68	4	6	34	30
10	5	42	42	8	0	74	82	7	9	29	22	5	6	123	119
1	6	99	83	10	0	67	72	0	10	52	51	8	6	55	53
2	6	24	9	12	0	71	69	2	10	49	45	10	6	60	69
3	6	78	73	1	1	401	423	4	10	46	56	12	6	46	48
5	6	68	69	2	1	214	211	1	11	81	58	1	7	148	146
6	6	61	71	3	1	205	198	3	11	61	65	3	7	139	137
7	6	37	32	5	1	91	93	6	11	32	24	4	7	54	64
9	6	49	61	7	1	55	63	1	12	32	27	5	7	75	80
10	6	46	50	8	1	42	40	4	12	33	33	6	7	48	43
1	7	180	177	9	1	31	30	1	13	66	76	2	8	35	30
2	7	68	65	10	1	45	40	3	13	42	50	3	8	28	30
3	7	82	82	0	2	184	180	5	13	40	35	4	8	45	45
4	7	65	59	1	2	73	66	0	14	46	46	6	8	29	27
5	7	60	56	2	2	28	37	2	14	30	26	8	8	48	49
7	7	58	66	3	2	134	125	1	15	64	66	9	8	45	41
10	7	57	54	5	2	27	44	3	15	38	36	10	8	48	48
3	8	106	103	6	2	63	54					1	9	108	102
5	8	74	78	7	2	42	60		L=	5		2	9	41	52
6	8	37	40	8	2	49	54					3	9	69	70
7	8	30	38	9	2	33	27	2	1	143	148	5	9	64	68
8	8	31	33	10	2	52	58	3	1	106	105	7	9	48	50
9	8	45	38	12	2	50	51	4	1	49	43	8	9	31	28
10	8	39	42	1	3	128	116	5	1	25	40	2	10	28	23
1	9	111	117	3	3	242	241	6	1	86	101	7	10	38	32
2	9	43	46	5	3	97	98	2	2	90	95	3	11	58	64
3	9	66	72	6	3	63	60	3	2	121	114	5	11	53	58
4	9	70	64	1	4	110	106	4	2	43	40	2	12	29	25
5	9	56	62	2	4	52	56	5	2	33	37	8	12	34	24
6	9	50	41	3	4	40	38	7	2	69	71	3	13	42	48
7	9	36	33	4	4	65	67	8	2	41	45	2	14	34	36
0	10	46	41	5	4	44	45	12	2	32	29	0	16	50	48
3	10	52	47	7	4	27	30	1	3	43	58	2	16	40	45
4	10	35	33	8	4	39	41	2	3	81	75				
5	10	69	71	10	4	40	39	3	3	117	111		L=	6	
6	10	33	25	12	4	43	47	4	3	29	26				
7	10	47	39	1	5	82	78	5	3	136	128	0	0	88	52
8	10	31	34	2	5	66	58	6	3	42	46	1	0	162	168
1	11	51	62	3	5	212	201	8	3	39	27	2	0	146	156
3	11	53	61	5	5	56	55	9	3	34	29	3	0	116	105
5	11	46	43	6	5	39	36	0	4	130	117	4	0	49	55
6	11	31	22	3	6	27	21	1	4	35	35	5	0	74	70
2	12	36	39	4	6	26	24	7	4	43	35	6	0	123	123
4	12	33	43	5	6	63	68	8	4	49	45	7	0	81	85

Table 3. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
8	0	66	57	0	10	39	35	6	5	91	94	4	0	158	160
9	0	68	67	2	10	61	62	7	5	32	33	5	0	37	33
10	0	41	36	3	10	40	53	8	5	33	41	6	0	120	125
11	0	32	20	5	10	50	61	10	5	35	38	7	0	91	90
12	0	48	43	7	10	37	35	0	6	71	71	8	0	40	32
1	1	295	315	1	11	41	46	2	6	72	76	9	0	70	68
2	1	228	231	3	11	34	34	3	6	63	58	1	1	53	42
4	1	133	128	4	11	67	75	4	6	51	48	2	1	64	62
5	1	81	76	6	11	67	69	5	6	83	82	3	1	106	112
6	1	84	85	1	12	33	29	6	6	33	40	4	1	81	90
7	1	51	59	2	12	31	34	7	6	69	79	5	1	49	51
8	1	62	71	3	12	43	43	8	6	57	64	6	1	77	87
10	1	46	35	5	12	71	70	9	6	44	49	7	1	92	93
0	2	59	65	7	12	38	44	2	7	63	69	8	1	33	32
1	2	36	13	1	13	57	56	3	7	38	38	9	1	69	85
2	2	71	75	2	13	44	51	4	7	68	85	11	1	50	48
3	2	71	80	3	13	29	31	5	7	33	40	13	1	38	40
4	2	154	146	4	13	33	32	6	7	48	48	0	2	141	173
6	2	37	26	6	13	36	33	7	7	38	40	1	2	31	38
7	2	75	60	0	14	30	26	8	7	50	54	2	2	122	127
9	2	47	45	3	14	34	30	0	8	140	140	3	2	32	39
10	2	43	36	1	15	60	54	1	8	60	56	4	2	132	135
12	2	36	31	3	15	36	35	2	8	81	86	5	2	106	113
1	3	32	37					3	8	69	47	6	2	90	91
2	3	123	126		L=	7		4	8	55	55	7	2	89	83
3	3	87	89					5	8	27	25	9	2	46	44
4	3	149	149	1	1	55	60	6	8	38	44	1	3	82	87
5	3	111	110	2	1	103	109	7	8	60	64	2	3	90	93
6	3	31	36	3	1	67	69	8	8	44	41	3	3	26	22
7	3	64	60	5	1	37	30	9	8	61	66	4	3	51	54
8	3	47	39	9	1	37	32	1	9	29	22	6	3	88	95
9	3	47	50	1	2	114	111	2	9	68	83	7	3	41	45
1	4	101	89	2	2	60	64	4	9	65	66	9	3	63	61
2	4	57	62	5	2	51	56	5	9	61	56	1	4	73	62
4	4	100	94	6	2	41	36	6	9	42	47	2	4	166	164
5	4	99	93	7	2	55	39	7	9	48	50	4	4	42	50
7	4	41	40	8	2	31	20	8	9	34	35	5	4	96	92
10	4	38	32	2	3	104	111	0	10	76	81	6	4	26	26
2	5	29	24	3	3	29	23	2	10	63	65	7	4	55	63
3	5	152	154	4	3	105	102	3	10	42	37	1	5	35	31
5	5	64	63	6	3	45	52	5	10	56	63	2	5	35	35
9	5	33	29	7	3	66	73	6	10	36	46	3	5	28	21
0	6	34	35	8	3	53	56	7	10	45	41	5	5	44	43
1	6	47	48	9	3	41	36	3	11	82	62	6	5	43	39
2	6	41	32	1	4	71	67	4	11	43	35	8	5	33	35
4	6	42	50	2	4	76	68	5	11	40	43	11	5	32	35
5	6	32	27	3	4	129	137	0	12	47	37	1	6	29	27
6	6	70	68	4	4	153	161	2	12	36	36	2	6	65	57
7	7	29	33	5	4	109	106	4	12	37	44	3	6	37	36
0	8	77	68	7	4	70	64	6	12	38	37	4	6	69	70
2	8	53	53	9	4	30	26	3	13	30	25	7	6	31	36
3	8	34	32	1	5	36	26					8	6	31	19
1	9	34	33	2	5	130	131		L=	8		1	7	44	42
4	9	41	47	3	5	42	35					3	7	41	36
7	9	42	42	4	5	144	144	1	0	142	138	0	8	62	49
8	9	45	38	5	5	47	51	3	0	108	104	2	8	37	47

Table 3. (Continued)

H	K	FO	FC
3	8	32	29
4	8	35	45
8	8	37	41
1	9	33	33
2	9	41	36
3	9	96	94
5	9	38	34
6	9	37	39
0	10	29	20
2	10	63	70
1	11	47	55
6	11	41	50
0	12	89	97
1	12	32	23
2	12	36	39
4	12	35	30
5	12	37	33
1	13	40	52
6	13	35	30
0	14	51	62
2	14	57	55
4	14	36	42
0	16	52	50
	L= 9		
2	1	73	80
5	1	23	23
6	1	29	36
8	1	38	30
9	1	33	30
11	1	34	18
1	2	49	48
2	2	123	124
4	2	109	106
8	2	42	50
1	3	39	40
2	3	43	44
3	3	98	101
5	3	37	30
7	3	41	46
9	3	55	54
11	3	38	33
0	4	69	66
1	4	22	23
2	4	170	172
3	4	45	38
4	4	119	116
6	4	45	42
8	4	30	23
1	5	64	74
2	5	39	41
3	5	48	49
6	5	46	39
7	5	39	36
9	5	45	43
11	5	46	52
0	6	204	205
1	6	30	33
2	6	118	115
4	6	80	89
6	6	62	64
8	6	33	25
12	6	33	32
1	7	102	106
3	7	44	51
4	7	30	24
7	7	35	42
9	7	53	56
11	7	58	67
0	8	199	196
1	8	26	26
2	8	124	129
4	8	52	51
6	8	71	75
1	9	56	58
4	9	30	36
5	9	40	41
9	9	33	35
11	9	39	37
0	10	113	122
2	10	66	66
6	10	30	37
2	12	46	44
4	12	47	51
1	13	31	36
1	15	48	53
	L=10		
0	0	223	209
2	0	282	285
3	0	45	54
4	0	103	96
5	0	119	113
6	0	62	64
7	0	76	76
8	0	64	56
1	1	79	79
2	1	233	245
3	1	42	53
4	1	84	83
5	1	53	51
6	1	58	55
7	1	105	110
9	1	37	34
11	1	57	49
13	1	42	43
0	2	219	218
2	2	181	184
3	2	75	71
4	2	25	13
5	2	100	99
6	2	101	95
7	2	30	32
8	2	75	82
1	3	38	37
3	3	166	161
4	3	124	128
5	3	37	37
6	3	71	78
9	3	42	36
0	4	93	88
1	4	38	32
2	4	46	55
3	4	79	80
4	4	100	93
6	4	56	52
7	4	61	59
8	4	35	33
9	4	31	29
3	5	39	40
7	5	42	40
8	5	37	35
9	5	44	48
1	6	25	17
2	6	24	21
4	6	58	57
6	6	31	32
1	7	51	57
5	7	27	38
2	8	64	68
7	8	31	25
8	8	37	52
1	9	89	93
5	9	33	29
6	9	31	25
0	10	75	66
2	10	52	50
3	10	28	38
5	10	33	42
1	11	56	65
4	11	36	43
6	11	53	55
8	11	34	29
0	12	48	53
2	12	56	61
3	12	43	41
5	12	51	53
7	12	33	32
1	13	36	40
2	13	37	37
3	13	30	32
4	13	30	18
0	14	63	66
2	14	53	57
4	14	37	37
0	16	55	54
	L=11		
1	1	43	46
2	1	28	25
3	1	34	35
6	1	31	30
1	2	56	69
4	2	44	51
5	2	62	70
6	2	33	28
7	2	66	79
8	2	32	32
2	3	67	73
4	3	51	67
5	3	64	78
6	3	99	104
2	4	49	53
3	4	53	59
4	4	71	63
5	4	126	123
7	4	92	95
1	5	23	17
2	5	38	46
3	5	23	41
4	5	139	143
6	5	120	111
1	6	34	43
2	6	59	56
3	6	65	68
4	6	49	47
5	6	73	77
6	6	47	63
7	6	91	100
9	6	43	52
1	7	44	47
2	7	78	81
3	7	59	62
4	7	72	72
6	7	55	63
8	7	56	67
9	7	47	63
10	7	41	40
0	8	86	82
4	8	30	28
5	8	38	51
6	8	66	65
7	8	46	57
8	8	31	27
9	8	41	45
2	9	55	68
4	9	53	57
6	9	41	36
7	9	48	54
8	9	62	63
2	10	39	35
4	10	65	63

Table 3. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
5	10	36	38	5	6	27	16	1	6	34	31	7	2	40	44
7	10	40	44	3	7	34	26	2	6	38	36	8	2	36	43
9	10	40	34	2	8	78	79	4	6	34	24	9	2	30	33
1	11	48	51	2	9	27	18	8	6	48	46	10	2	39	45
6	11	40	34	3	9	42	51	10	6	33	37	12	2	46	48
4	12	31	39	6	9	41	48	12	6	46	53	1	3	108	112
3	13	37	40	7	9	30	35	1	7	208	215	2	3	89	93
				0	10	33	29	2	7	26	33	3	3	136	154
	L=12			2	10	50	56	3	7	106	106	4	3	28	17
				7	10	32	37	5	7	47	51	5	3	109	106
0	0	52	60	1	11	49	48	7	7	41	45	8	3	40	39
1	0	49	45	2	11	41	48	0	8	98	104	1	4	81	84
3	0	89	98	4	11	43	55	2	8	49	40	2	4	48	51
5	0	108	111	6	11	46	47	6	8	42	40	3	4	62	68
7	0	96	95	0	12	47	50	8	8	41	43	5	4	80	100
9	0	56	59	3	12	44	52	10	8	42	43	8	4	45	41
10	0	48	49	1	13	43	62	1	9	143	147	10	4	43	39
1	1	78	96	3	13	48	34	2	9	57	73	1	5	70	68
2	1	156	149	6	13	37	23	3	9	61	66	3	5	53	58
3	1	47	34	1	15	47	46	5	9	43	50	4	5	28	40
4	1	98	98					1	10	51	46	5	5	60	72
5	1	123	122		L=13			3	10	43	41	2	6	31	34
6	1	78	81					4	10	41	45	5	6	34	38
7	1	59	68	1	1	43	45	1	11	59	56	3	7	30	32
8	1	43	52	2	1	43	42	3	11	54	65	7	7	32	27
0	2	69	62	3	1	75	83	6	12	32	32	0	8	73	79
1	2	83	78	7	1	37	41	2	13	30	30	1	8	46	55
2	2	77	68	0	2	59	57	3	13	42	44	2	8	66	63
3	2	48	44	1	2	91	99	5	13	31	32	4	8	36	32
5	2	129	135	2	2	115	119	0	14	39	43	1	9	90	82
7	2	67	73	3	2	97	106	2	14	34	41	2	9	31	25
8	2	50	57	5	2	32	46	2	16	32	36	3	9	31	30
10	2	53	53	6	2	34	43					9	9	33	31
12	2	34	29	7	2	30	18		L=14			0	10	62	54
1	3	33	37	8	2	52	55					2	10	45	45
2	3	87	76	9	2	33	24	1	0	119	109	3	10	34	31
3	3	125	137	1	3	82	81	3	0	144	151	4	10	35	38
4	3	124	122	2	3	41	42	4	0	31	21	1	11	60	44
5	3	110	105	3	3	223	215	5	0	62	53	3	11	40	46
6	3	82	93	4	3	72	83	6	0	48	47	2	12	38	36
0	4	58	40	5	3	40	41	7	0	33	37	1	13	57	66
1	4	51	43	6	3	41	37	8	0	48	57	3	13	58	58
2	4	26	10	0	4	81	64	9	0	29	43	0	14	45	42
3	4	44	39	2	4	47	53	10	0	46	59	1	15	51	53
4	4	84	78	4	4	26	21	12	0	49	51				
5	4	31	29	7	4	31	18	1	1	146	148		L=15		
7	4	59	59	8	4	38	41	2	1	40	45				
8	4	30	26	10	4	32	31	3	1	196	197	1	1	28	28
9	4	44	46	12	4	36	40	5	1	133	131	4	1	58	63
2	5	100	104	1	5	138	138	6	1	58	60	6	1	27	28
3	5	58	64	2	5	98	99	7	1	33	38	9	1	29	18
5	5	44	45	3	5	89	98	1	2	83	86	2	2	34	26
7	5	42	34	4	5	50	52	2	2	37	38	4	2	25	19
2	6	45	50	5	5	79	79	3	2	164	163	5	2	34	39
3	6	30	33	6	5	32	19	5	2	43	41	7	2	56	58
4	6	32	37	0	6	115	117	6	2	48	50	1	3	76	70

Table 3. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
2	3	39	40		L=16			3	12	65	71	7	10	32	25
3	3	124	122					4	12	32	35	1	11	49	38
4	3	73	71	0	0	228	222	0	14	42	35	7	11	32	28
5	3	38	29	2	0	98	101	3	14	34	34	0	12	34	28
6	3	56	72	3	0	153	151	4	14	32	30	1	12	41	28
7	3	39	38	5	0	98	98					2	12	45	46
8	3	38	33	6	0	79	73		L=17			4	12	43	42
0	4	51	64	7	0	45	31								
1	4	58	60	8	0	57	68	1	1	55	50		L=18		
4	4	32	15	11	0	34	34	3	1	57	57				
5	4	92	106	1	1	93	89	5	1	27	28	0	0	284	279
6	4	56	45	3	1	78	75	7	1	42	39	1	0	55	35
7	4	88	92	4	1	147	149	10	1	31	22	2	0	201	204
1	5	41	44	6	1	75	73	0	2	104	89	3	0	43	39
2	5	32	30	10	1	45	52	1	2	37	40	4	0	58	62
3	5	83	80	11	1	38	31	2	2	91	94	1	1	31	30
4	5	55	56	1	2	66	65	3	2	36	41	2	1	61	58
5	5	41	42	2	2	113	114	4	2	49	54	3	1	68	71
6	5	73	75	3	2	90	84	5	2	56	61	9	1	60	64
8	5	78	82	4	2	66	56	9	2	29	17	10	1	31	26
10	5	32	30	5	2	88	85	1	3	70	69	11	1	59	70
1	6	48	44	6	2	73	72	2	3	44	43	0	2	251	247
2	6	36	26	7	2	48	57	4	3	26	32	1	2	29	32
3	6	64	66	9	2	34	35	6	3	43	41	2	2	136	141
4	6	34	29	1	3	87	86	9	3	34	21	4	2	81	90
5	6	88	96	2	3	167	169	0	4	137	139	6	2	36	37
7	6	70	76	3	3	64	59	1	4	35	42	9	2	31	29
1	7	102	108	4	3	44	31	2	4	91	100	2	3	36	31
2	7	67	78	6	3	59	42	4	4	53	54	3	3	46	54
3	7	27	28	8	3	60	76	5	4	96	101	4	3	28	36
4	7	41	33	2	4	85	90	6	4	59	56	5	3	27	24
5	7	58	57	3	4	26	18	7	4	41	36	6	3	40	42
6	7	51	48	4	4	87	112	1	5	38	36	9	3	44	54
7	7	42	36	5	4	68	78	2	5	56	55	11	3	39	40
8	7	61	66	6	4	36	35	4	5	35	38	0	4	115	105
1	8	66	74	7	4	59	58	6	5	56	60	2	4	82	101
3	8	82	77	1	5	84	79	11	5	48	42	3	4	38	48
4	8	31	32	2	5	71	74	0	6	192	199	4	4	89	103
5	8	32	28	3	5	30	31	2	6	148	145	4	5	40	35
7	8	47	53	1	7	81	76	3	6	57	57	7	5	33	31
9	8	33	41	6	7	29	29	4	6	76	83	9	5	32	44
10	8	34	36	8	7	40	28	5	6	47	41	1	6	36	25
1	9	74	67	0	8	43	33	6	6	29	14	2	6	40	39
3	9	37	41	2	8	34	41	7	6	40	44	6	6	38	28
4	9	36	42	4	8	34	32	1	7	62	44	3	7	31	39
5	9	30	25	6	9	51	38	4	7	30	17	1	8	27	15
6	9	35	42	1	10	31	36	7	7	37	33	1	9	81	92
7	9	32	28	2	10	46	36	8	7	31	26	2	10	41	42
8	9	38	41	4	10	34	29	0	8	201	195	3	11	52	58
10	9	36	30	2	11	61	57	2	8	121	128	0	12	32	29
2	10	31	23	3	11	33	30	4	8	44	43	2	12	53	57
7	10	35	37	4	11	52	58	6	8	35	33	4	12	55	67
9	10	36	33	6	11	43	51	1	9	36	20	1	13	36	37
3	11	34	40	8	11	37	39	0	10	73	71	0	14	60	75
5	11	38	29	1	12	36	28	2	10	71	75	2	14	53	62
4	12	36	24	2	12	36	43	4	10	64	67	0	16	40	34

CHAPTER III

RESULTS AND DISCUSSION

Cobalt Complex of Salicylideneglycinate

In 1950 Ray and Mukherjee (39) reported the preparation of a number of first row transition metal complexes with Schiff bases of salicylaldehyde and amino acids. Of particular interest was a cobalt complex reported to have a ratio of 1:1:2 for cobalt:salicylaldehyde:glycine and exhibiting a room temperature magnetic moment of 2.89 B.M., which is low for high-spin d^7 cobalt(II) in an octahedral crystal field. One explanation for this low magnetic moment could be that the actual structure of the complex consists of oxygen-bridged polynuclear units. In order to verify this, the complex was prepared according to the published method, analyzed for carbon, hydrogen and nitrogen content, and subjected to a single-crystal x-ray structure determination.

The analyses revealed that the cobalt compound should have been formulated with a 3:4:4 ratio of cobalt:salicylaldehyde:glycine. A subsequent x-ray study corroborated this ratio, and revealed the complete formulation of the complex; namely, $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$ (where SALGLY is the dianion of the imine of salicylaldehyde and glycine). In addition, the magnetic moment of the complex, calculated on the basis of this formulation ($\mu_{eff}^{298^\circ K} = 5.16$ B.M.), is consistent with that expected for one octahedral cobalt(II) (17) per formula unit (see ch. II, p. 129). As a result of both x-ray and magnetic studies, the complex is best de-

scribed as consisting of hydrogen-bonded trimeric units, containing one paramagnetic cobalt(II) ion, octahedrally coordinated by six aquo ligands, and two diamagnetic cobalt(III) ions, each octahedrally coordinated by two divalent tridentate SALGLY ligands. Each SALGLY ligand is coordinated such that the azomethine nitrogens are trans to each other, the phenolic oxygen of each ligand is trans to the carboxyl oxygen of the same ligand, and the carboxyl oxygens are directed toward the central cobalt(III) ion.

Equivalent cobalt(II) ions are some 6.07Å from the nearest cobalt(III) ion, and occupy positions in the cell that are coincident with the twofold rotation axes of Pbcn as depicted in the perspective drawing in Figure 1. There is an obvious axial distortion in the octahedral coordination sphere of the cobalt(II) ion. The metal-to-donor oxygen distances are: 2.05(1)Å, Co2-OW1; 2.13(1)Å, Co2-OW2; and, 2.02(1)Å, Co2-OW3. The angles at cobalt for cis-donor oxygens are: 86.4(4)°, OW1-Co2-OW2; 89.5(4)°, OW1-Co2-OW3; and, 91.0(4)°, OW2-Co2-Ow3. This distortion is probably due to hydrogen bonding (to be discussed later).

The cobalt(III) ion, which is coordinated by two tridentate SALGLY ligands, shows some distortion from ideal octahedral geometry. Although the metal-to-donor atom distances range from 1.86(1)Å to 1.96(1)Å, and the angles at cobalt for cis donor atoms range from 95.3° to 84.2°, these distortions from octahedral coordination are not deemed significantly large, from the standpoint of spectral and magnetic properties.

It is interesting to compare the structural features of the two SALGLY ligands bound to cobalt(III). Table 4 lists selected bond dis-

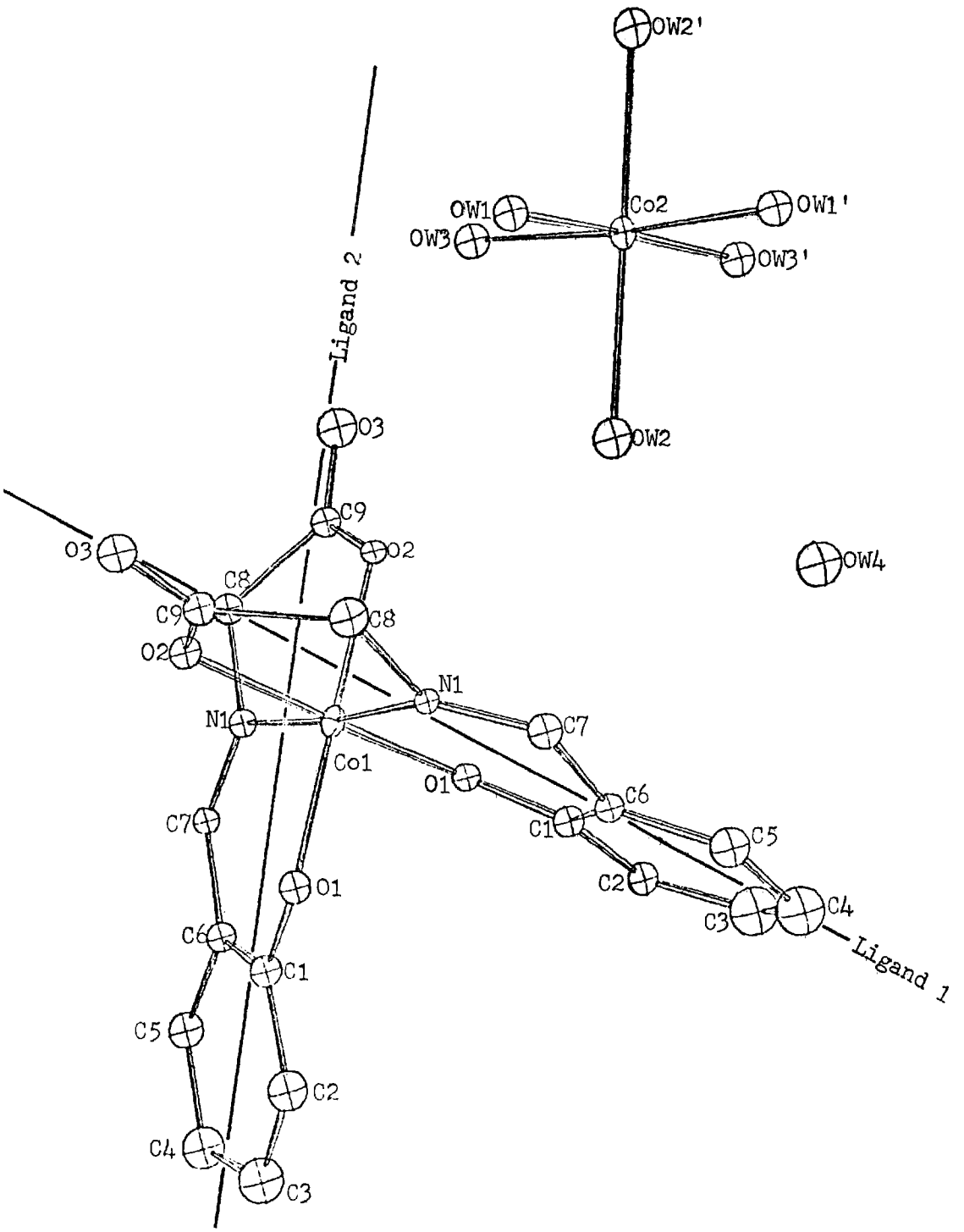


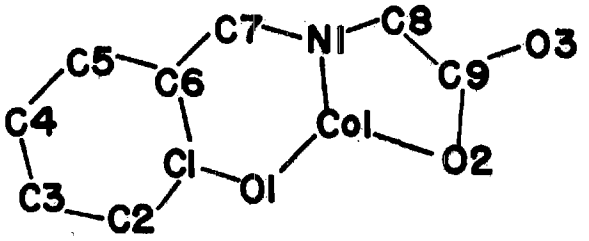
Figure 1. Perspective Drawing of $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$

tances and angles for the $[Co(SALGLY)_2]^-$ moiety. The ligand units appear identical when comparing interatomic distances and angles between corresponding atom pairs. There are only two such atom pairs per ligand unit whose interatomic distances do not agree to within one estimated standard deviation; namely, the Co1-O1 pair (1.86(1)Å, 1.90(1)Å) and the C8-N1 pair (1.50(2)Å, 1.43(2)Å). On the other hand, even these interatomic distances compare favorably within four standard deviations.

Although the two ligand units appear to have identical interatomic distances, the two ligands are not identical in terms of the degree of their planarity. Tables 5 and 6 give the equations of the least-squares planes in the $[Co(SALGLY)_2]^-$ unit and deviations of the ligand atoms from these planes. Table 6 clearly indicates that when one compares the deviations of the atoms of ligand 1 and ligand 2, P1(L1) and P1(L2), from their respective NO_2 coordination planes, L1 and L2, the atoms in ligand 1 deviate much less than those of ligand 2. Furthermore, the average deviations from the planes listed in Table 6 are consistently less for the atoms of ligand 1 than for the atoms of ligand 2. In addition, the five- and six-membered chelate rings[1] in ligand 1 are much less distorted from planarity, P2(L1), than the corresponding chelate rings of ligand 2, P2(L2). This can be obtained from the equations in Table 5, from which one can calculate the dihedral angle between the planes defined by the five- and six-membered chelate rings of ligand 1 is 171.65°, while that of ligand 2 is 164.59°. Obviously, then, there

[1]When referring to planes described as being either the five- or six-membered chelate rings, the atoms defining the planes do not include the atoms from any groups attached to the chelate rings.

Table 4. Interatomic Distances (Å) and Angles (°) for $[Co(SALGLY)_2]^-$



ATOMS	Distance, Å Ligand 1	Ligand 2
Co1 - O1	1.86(1)	1.90(1)
Co1 - O2	1.95(1)	1.96(1)
Co1 - N1	1.93(1)	1.92(1)
O1 - C1	1.30(2)	1.31(2)
C1 - C2	1.39(2)	1.35(2)
C2 - C3	1.35(2)	1.28(2)
C3 - C4	1.31(2)	1.45(3)
C4 - C5	1.45(2)	1.36(2)
C5 - C6	1.38(2)	1.37(2)
C6 - C1	1.45(2)	1.41(2)
C6 - C7	1.41(2)	1.40(2)
C7 - N1	1.26(2)	1.25(2)
C8 - N1	1.50(2)	1.43(2)
C8 - C9	1.53(2)	1.55(2)

Table 4. (Continued)

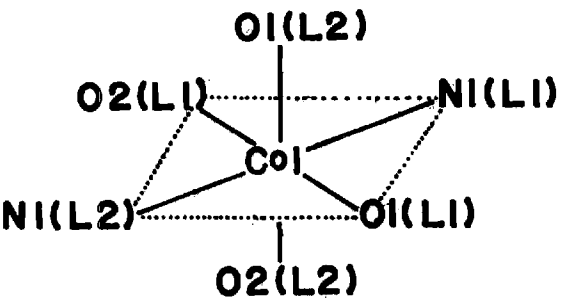
ATOMS	Distance, Å Ligand 1	Ligand 2
C9 - O2	1.32(2)	1.29(2)
C9 - O3	1.19(2)	1.21(2)

ATOMS	Angles, ° Ligand 1	Ligand 2
N1 - Co1 - O2	87.4(5)	84.2(4)
N1 - Co1 - O1	94.2(5)	95.3(4)
Co1 - O2 - C9	115.0(10)	115.6(10)
O2 - C9 - C8	114.0(14)	113.5(15)
C9 - C8 - N1	113.4(13)	109.6(13)
C8 - N1 - C7	123.3(13)	127.8(12)
C8 - N1 - Co1	108.2(9)	112.4(9)
N1 - C7 - C6	120.6(15)	132.1(15)
C7 - N1 - Co1	127.7(11)	119.8(11)
O2 - C9 - O3	124.0(15)	125.2(16)
C8 - C9 - O3	121.8(15)	120.0(16)
C7 - C6 - C1	124.3(14)	121.0(15)
C7 - C6 - C5	114.2(14)	123.2(16)
C5 - C6 - C1	120.1(15)	115.7(17)

Table 4. (Continued)

ATOMS	Angles, ° Ligand 1	Ligand 2
C6 - C1 - C2	118.2(15)	124.1(17)
C1 - C2 - C3	119.1(17)	115.6(19)
C2 - C3 - C4	125.1(22)	124.7(19)
C3 - C4 - C5	118.5(21)	113.2(19)
C4 - C5 - C6	118.2(16)	125.8(20)
C6 - C1 - O1	123.7(14)	122.9(15)
C2 - C1 - O1	118.0(14)	113.0(16)
C1 - O1 - Co1	124.4(9)	123.8(9)
O1 - Co1 - O2	177.3(5)	178.7(4)

ATOMS[a]	Angles, °
O1(L1) - Co1 - O1(L2)	89.8(4)
O1(L1) - Co1 - O2(L2)	89.0(4)
O1(L1) - Co1 - N1(L2)	89.3(5)
N1(L1) - Co1 - O1(L2)	89.1(5)
N1(L1) - Co1 - O2(L2)	91.4(5)
N1(L1) - Co1 - N1(L2)	174.3(6)
O2(L1) - Co1 - O1(L2)	92.4(4)
O2(L1) - Co1 - O2(L2)	88.7(4)
O2(L1) - Co1 - N1(L2)	88.9(5)



[a]The appearance of either "L1" or "L2" with the atom name means that the atom referred to appears in Ligand 1 or Ligand 2 respectively. For example, C1(L1), refers to carbon 1 in ligand unit 1.

Table 5. Least-Squares Planes in the $[Co(SALGLY)_2]^-$ Moiety

Coefficients of least-squares plane equation[a] : $AZ + BY + CZ + D = 0$

Label	Description	A	B	C	D
P1(L1)	(Coordination plane defined by Co1, N1, O1, and O2 of Ligand 1)	0.5038	0.2338	0.8316	-4.548
P1(L2)	(Coordination plane defined by Co1, N1, O1 and O2 of Ligand 2)	-0.6996	-0.4645	0.5430	-2.268
P2(L1)	(Plane defined by the six-membered chelate ring[b] of Ligand 1)	0.5975	0.2378	0.7658	-4.324
P2(L2)	(Plane defined by the six-membered chelate ring[b] of Ligand 2)	-0.8287	-0.3799	0.4110	-1.735
P3(L1)	(Plane defined by the five-membered chelate ring[b] of Ligand 1)	0.4964	0.3370	0.8000	-4.358
P3(L2)	(Plane defined by the five-membered chelate ring[b] of Ligand 2)	-0.6501	-0.5207	0.5533	-2.316
P4(L1)	(Benzene ring in Ligand 1)	0.6302	0.2075	0.7482	-4.276
P4(L2)	(Benzene ring in Ligand 2)	-0.8942	-0.3882	0.2230	-1.173

Table 5. (Continued)

[a]The equations are referred to orthogonal axes with the orthogonal X axis coincident to a and the orthogonal Z axis coincident to c^*.

[b]The planes defined by the atoms of the five- or six-membered chelate rings do not include any atoms of groups attached to the chelate ring.

Table 6. Normal Distances (Å) from the Planes[a] Describe in Table 5

ATOM	P1(L1)	P1(L2)	P2(L1)	P2(L2)	P3(L1)	P3(L2)	P4(L1)	P4(L2)
Co1	(-0.0236)	(0.0117)	(-0.0979)	(-0.1316)	(0.0533)	(0.0075)	-0.1420	-0.5532
C1	-0.2890	-0.4846	(-0.0424)	(-0.0933)	-0.1468	-0.6054	(0.0093)	(0.0294)
C2	-0.4702	-0.8951	-0.0915	-0.3587	-0.2261	-1.0110	(-0.0242)	(0.0113)
C3	-0.6015	-1.4261	-0.0863	-0.6222	-0.4043	-1.6256	(0.0434)	(-0.0425)
C4	-0.7590	-1.4670	-0.2224	-0.5265	-0.6943	-1.7650	(-0.0453)	(0.0116)
C5	-0.5428	-1.0175	-0.1342	-0.2427	-0.5903	-1.3120	(0.0303)	(0.0374)
C6	-0.3790	-0.6132	(-0.1160)	(-0.1153)	-0.3871	-0.8220	(-0.0150)	(-0.0533)
C7	-0.0364	-0.2619	(0.1080)	(0.0792)	-0.1614	-0.4736	0.2004	-0.1177
C8	0.3232	0.2990	0.2021	0.2388	(0.0988)	(0.1496)	0.2292	-0.4358
C9	0.1452	-0.0151	-0.1395	-0.3792	(-0.0307)	(-0.0606)	-0.1833	-1.2573
O1	(0.0117)	(-0.0062)	(0.1289)	(0.1341)	0.2002	-0.0441	0.1188	0.0720

Table 6. (Continued)

ATOM	P1(L1)	P1(L2)	P2(L1)	P2(L2)	P3(L1)	P3(L2)	P4(L1)	P4(L2)
O2	(0.0114)	(-0.0057)	-0.2673	-0.4423	(-0.0233)	(0.0243)	-0.3502	-1.2375
O3	0.2594	-0.008	-0.1388	-0.5136	-0.0018	-10.0414	-0.1977	-1.6138
N1	(0.003)	(0.0001)	(0.0062)	(0.0860)	(-0.1037)	(-0.1409)	0.0437	-0.3320
Average Distance from Plane								
	-0.1679	-0.4202	-0.0636	-0.2062	-0.1727	-0.5514	-0.0202	-0.3915

[a]( ) indicates that the atom was used in the calculation of the least-squares plane.

are limitations on the degree of structural similarity between ligand 1 and ligand 2.

Allowing for these distortions, however, both ligands are exceedingly similar to the extent that they each provide oxygen atoms which participate in hydrogen bonding, and in so-doing, enhance the overall stability of the trimer units. Inspection of the structural arrangement of the uncoordinated carboxyl oxygens of the SALGLY ligands reveals that they are strongly hydrogen-bonded to aquo ligands of the complex, $[Co(H_2O)_6]^{2+}$; namely, O2(L2)-OW3, 2.66(1)Å; O3(L1)-OW1, 2.78(1)Å. On the other hand, these hydrogen bonds do not constitute an infinite network of any kind, but are confined to their respective trimeric units, $[Co(H_2O)_6][Co(SALGLY)_2]_2$, (i.e. the hydrogen-bonds are solely of the intratrimer type). A hydrogen bond is also formed between the coordinated carbonyl oxygen of ligand 2 and aquo ligand on cobalt(II), (O2(L2)-OW2, 2.91Å); the same aquo ligand is also strongly hydrogen bonded to a lattice water molecule, (OW2-OW4, 2.64(1)Å).

The strong hydrogen bonding observed in this complex could be an explanation for the greater distortions from planarity of ligand 2. Interestingly enough, the hydrogen-bonded oxygen-oxygen contacts between the carboxyl oxygens on ligand 2 and water molecules on cobalt(II) are more than 0.10Å shorter than those on ligand (i.e. O2(L2)-OW3, 2.66(1)Å and O3(L1)-OW1, 2.78(1)Å). Furthermore, additional hydrogen bonding of O2(L2) to a second water molecule, OW2, is another source of distortion for ligand 2 that is not found for ligand 1. To aid in visualizing these features of the structure, the packing is illustrated in Figure 2.

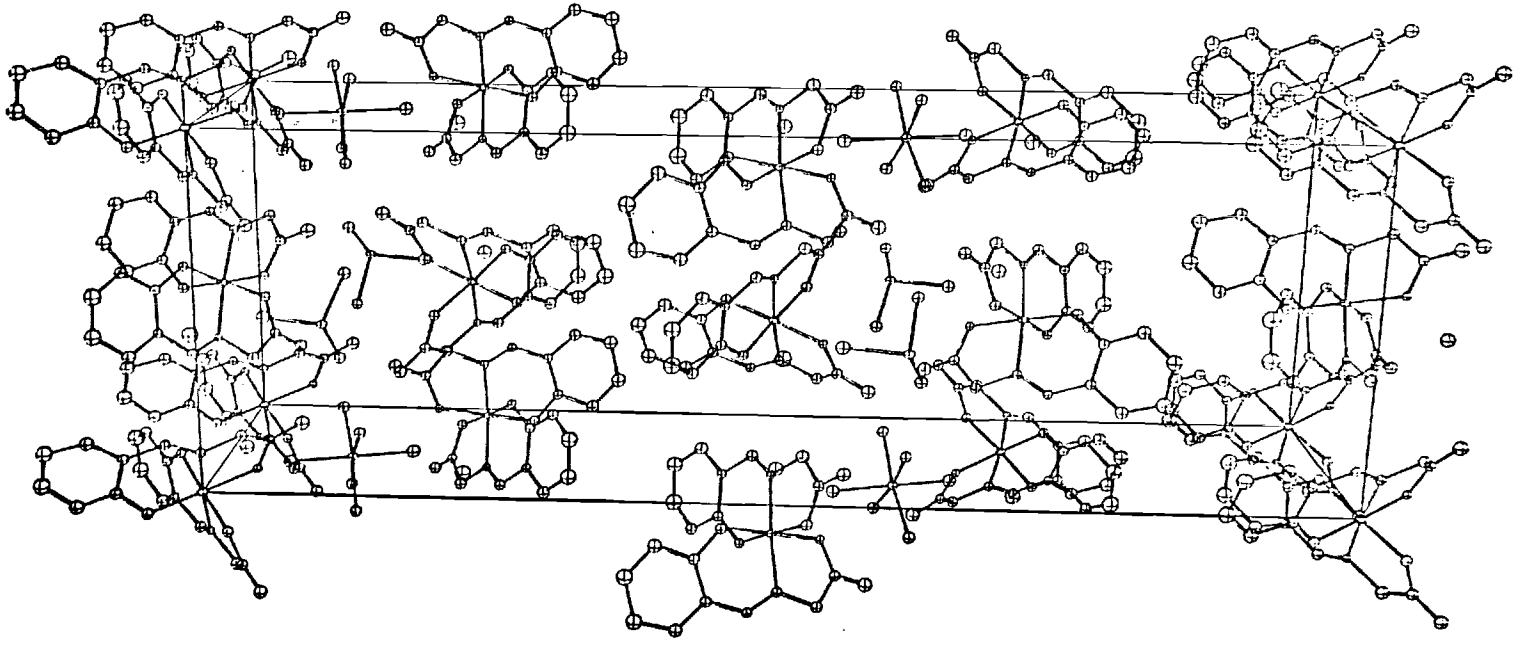


Figure 2. Packing Diagram for $[Co(H_2O)_6][Co(SALGLY)_2]_2 \cdot 2H_2O$

Iron Complex of Salicylideneglycinate

Since the analysis of the cobalt salicylideneglycinate complex did not agree with that reported by Ray and Mukherjee for the same complex, it raised questions about their analyses of the other salicylideneglycinate complexes, particularly those with iron and manganese. These compounds were of special interest because both metal ions have reasonably stable +2 and +3 oxidation states and could form mixed-oxidation state complexes similar to that found for cobalt salicylideneglycinate. As a result, the iron complex was prepared and submitted for analysis. Indeed, the analysis did not agree with that reported by Ray and Mukherjee, but suggested a mixed oxidation state complex with the formulation, $[Fe(H_2O)_6][Fe(SALGLY)_2]_2 \cdot 2H_2O$. Because of the relatively small difference in the magnetic moments of iron(II) and iron(III) complexes, there is less conclusive evidence for the divalent oxidation state from magnetic studies. Nevertheless, J. L. Breece (15), who observed a magnetic moment for the complex of 9.91 B.M. per formula unit, was able to subtract out the susceptibility due to the two iron(III) ions in the complex using the χ_m values obtained by Bailer (44) for $NaFe(SALGLY)_2$, and showed that the resultant magnetic moment of 5.35 B.M. was consistent with that expected for an iron(II) ion.[2] Subsequent x-ray studies by Breece (15), however, indicated that the iron complex crystallized in the space group $P2_1/c$ rather than the space group, Pbcn, observed for the cobalt complex. In order to verify the formulation suggested by chemical analyses and substantiated by magnetic studies, and to determine the

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[2]The range of experimental μ_{eff} for iron(II) is 5.1-5.5 B.M. (17).

nature of the trimeric unit (i.e. whether it is an oxygen-bridged trimeric unit, a hydrogen-bridged trimeric unit, or some other unit), Breece (15) conducted a complete x-ray structure determination of the iron complex.

The structure of the complex is quite similar to that found for the cobalt complex, despite the obvious difference in the morphology of the crystals. The iron(II) ion occupies a crystallographic inversion center as depicted in the perspective drawing in Figure 3 and is surrounded by a distorted octahedral arrangement of six waters. The three independent iron(II)-oxygen distances are 2.14Å, 2.11Å, and 2.11Å and the cis O-Fe(II)-O angles are 88.68°, 76.02°, 88.77°, 91.32°, 103.98°, and 91.23°. Also, the arrangement of the two SALGLY ligands around each iron(III) ion is a distorted octahedron with phenolic oxygen-iron(III) distances of 1.92Å, carboxy oxygen-iron(III) distances of 2.08Å and 2.07Å, and nitrogen-iron(III) distances of 2.07Å and 2.11Å. The SALGLY ligands are coordinated such that the azomethine nitrogens are trans to each other, the phenolic oxygen of each ligand is trans to the carboxyl oxygen of the same ligand, and the carboxyl oxygens are directed toward the central iron(III).

The closest approach of an iron(II) ion to an iron(III) ion is 5.61Å, but a hydrogen-bond (2.76Å) between an aquo oxygen, OW4, on iron(II) and a non-coordinated carboxyl oxygen, O3(L1), joins the iron(II) complex to the iron(III) complexes on either side of the inversion center. Additional hydrogen bonds (2.80Å) between an aquo oxygen, OW3, on iron(II) and a second non-coordinated carboxyl oxygen, O3(L2), attached to the iron(III) ion of an adjacent molecule, connect the

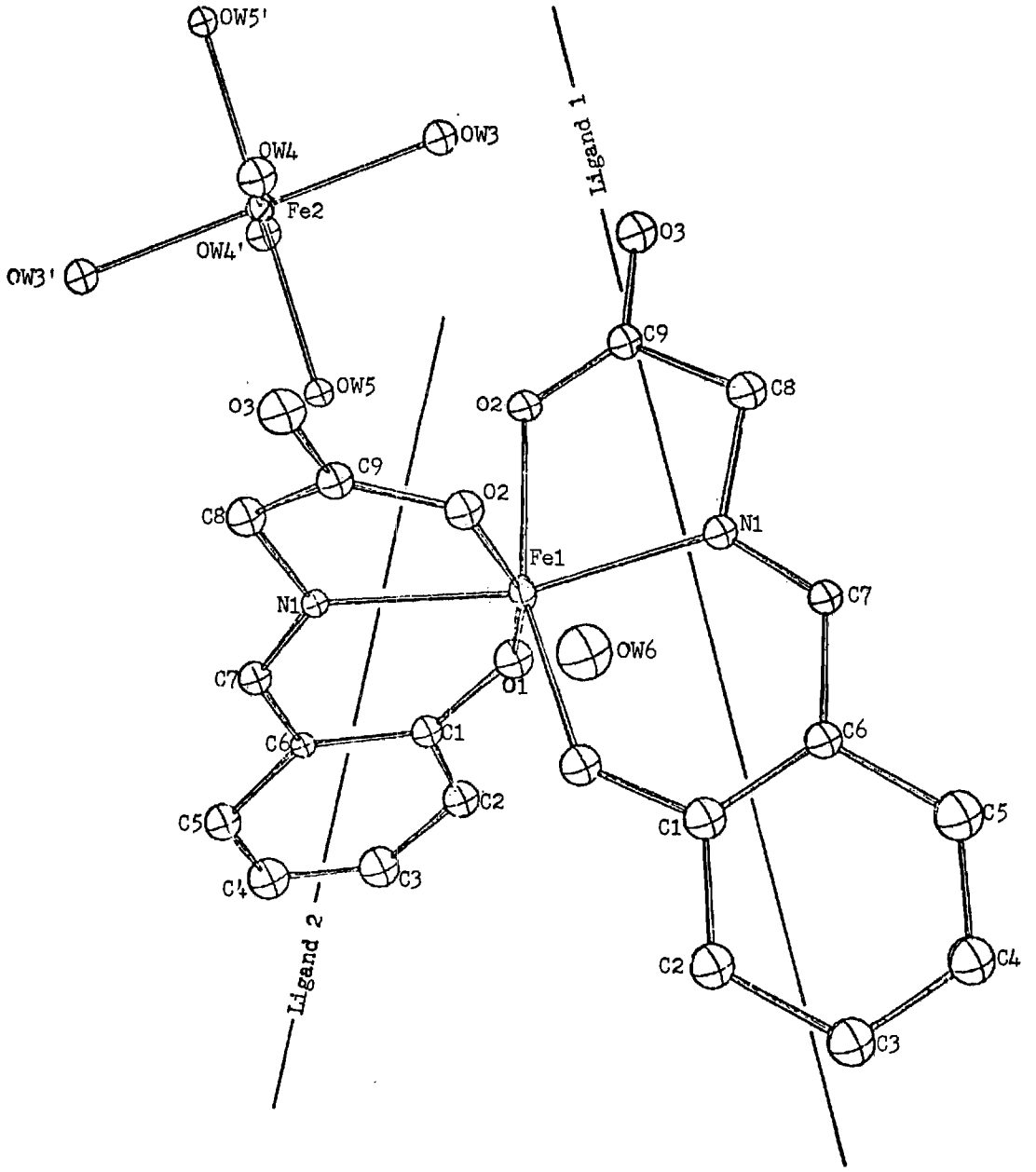

Figure 3. Perspective Drawing of $[Fe(H_2O)_6][Fe(SALGLY)_2]_2 \cdot 2H_2O$

complexes into infinite chains as shown in Figure 4. This infinite chain network is the major difference between the structures of the iron and cobalt salicylideneglycinate complexes. Although the cobalt and iron compounds have identical formulas, $[M(H_2O)_6][M(SALGLY)_2]_2 \cdot 2H_2O$, structurally the cobalt complex consists of individual trimeric units, whereas the iron complex consists of $[Fe(H_2O)_6]^{2+}$ and $[Fe(SALGLY)_2]^-$ moieties, hydrogen-bonded together to form infinite chains. Furthermore, the degree of distortion from planarity within each of the two ligands, L1 and L2, bound to Fe(III) are not distinctly different. Tables 7 and 8 give the equations for the least-squares planes and the normal distances from the planes for the atoms in the $[Fe(SALGLY)_2]^-$ moiety. Since the hydrogen-bonded oxygen-oxygen contacts between carboxyl oxygens on Fe(III) and water molecules on Fe(II) do not differ by more than 0.04Å (O3(L1)-OW4, 2.76Å and O3(L2)-OW3, 2.80Å), there would be no additional distorting forces operating on ligand 1 that were not operating on ligand 2. Consequently, the distortions from planarity of ligands 1 and 2 are comparable in $[Fe(SALGLY)_2]^-$, but distinctly different in $[Co(SALGLY)_2]^-$ due to the unequal hydrogen bonding forces operating on ligand 1 and ligand 2.

Manganese Complexes of Salicylideneglycinate

Two manganese salicylideneglycinate complexes were prepared and characterized. One was found to have a formula similar to both the cobalt and iron compounds; namely, $[Mn(H_2O)_6][Mn(SALGLY)_2]_2 \cdot 2H_2O$. An x-ray study of this crystal revealed that it was isomorphous with the iron crystal (space group $P2_1/c$). The cell parameters obtained from

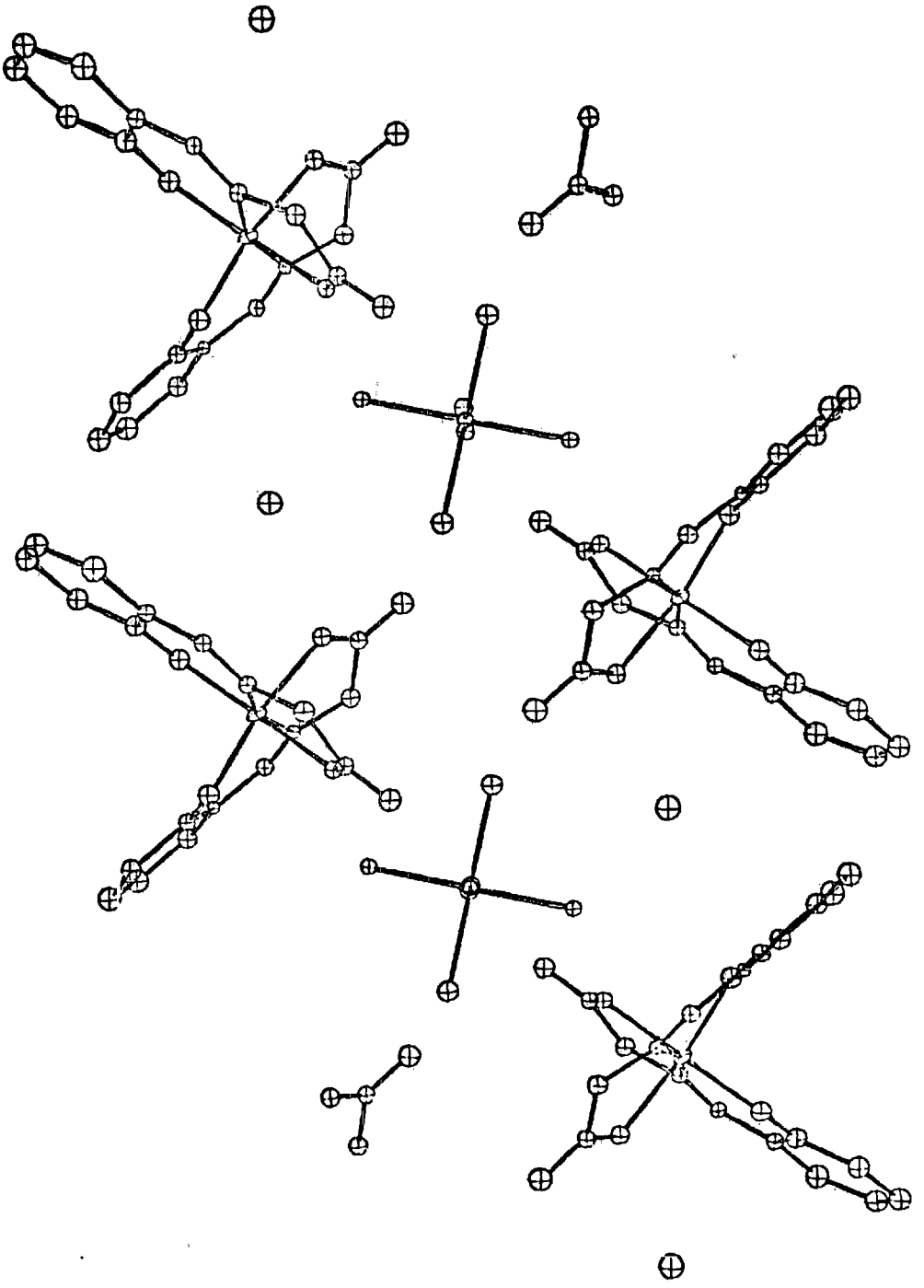

Figure 4. Packing Diagram for $[Fe(H_2O)_6][Fe(SALGLY)_2]_2 \cdot 2H_2O$

Table 7. Least-Squares Planes in the $[Fe(SALGLY)_2]^-$ Moiety

Coefficients of least-squares plane equation[a]: $AX + BY + CZ + D = 0$

Label	Description	A	B	C	D
P1(L1)	(Coordination plane defined by Fe1, N1, O1 and O2 of Ligand 1)	0.6112	0.3068	0.7296	-10.95
P1(L2)	(Coordination plane defined by Fe1, N1, O1 and O2 of Ligand 2)	-0.7796	0.3969	0.4844	9.233
P2(L1)	(Plane defined by the six-membered chelate ring[b] of Ligand 1)	0.5585	0.3149	0.7674	-10.41
P2(L2)	(Plane defined by the six-membered chelate ring[b] of Ligand 2)	-0.7328	0.2692	0.6249	8.164
P3(L1)	(Plane defined by the five-membered chelate ring[b] of Ligand 1)	0.6352	0.3212	0.7023	-11.20
P3(L2)	(Plane defined by the five-membered chelate ring[b] of Ligand 2)	-0.7054	0.5062	0.4962	8.099
P4(L1)	(Benzene ring in Ligand 1)	0.4762	0.3608	0.8019	-9.562
P4(L2)	(Benzene ring in Ligand 2)	-0.6671	0.1689	0.7253	7.232

Table 7. (Continued)

[a]The equations are referred to orthogonal axes with the orthogonal X axis coincident to a and the orthogonal Z axis coincident to c^*.

[b]The planes defined by the atoms of the five- or six-membered chelate rings do not include any atoms of groups attached to the chelate rings.

Table 8. Normal Distances (Å) from the Planes[a] Described in Table 7

ATOM	P1(L1)	P1(L2)	P2(L1)	P2(L2)	P3(L1)	P3(L2)	P4(L1)	P4(L2)
Fe1	(0.0446)	(0.0345)	(-0.0066)	(0.1658)	(0.0248)	(-0.0657)	-0.1932	0.5432
C1	-0.1895	0.4429	(-0.0531)	(0.0518)	-0.3212	0.3106	(-0.0065)	(-0.0013)
C2	-0.3949	0.7441	-0.1723	0.2026	-0.5603	0.4889	(0.0160)	(0.0084)
C3	-0.5617	1.2028	-0.2638	0.3971	-0.7838	1.099	(-0.0045)	(-0.0130)
C4	-0.4886	1.4166	-0.2051	0.4976	-0.7308	1.3949	(-0.0193)	(0.0106)
C5	-0.2225	1.1630	-0.0212	0.3665	-0.4322	1.2646	(0.0293)	(-0.0029)
C6	-0.1106	0.6697	(0.0117)	(0.1446)	-0.2625	0.7167	(-0.0152)	(-0.0016)
C7	-0.0104	0.3782	(0.0276)	(-0.0280)	-0.1309	0.5489	-0.1406	-0.0584
C8	-0.1183	-0.4272	0.0025	-0.5047	(0.0734)	(-0.1344)	-0.3877	-0.2387
C9	-0.0574	-0.2529	-0.2519	-0.0532	(-0.0429)	(-0.0084)	-0.7144	0.4239
O1	(-0.0280)	(-0.0200)	(0.0449)	(-0.1588)	-0.1092	-0.2172	0.0368	-0.0058

Table 8. (Continued)

ATOM	P1(L1)	P1(L2)	P2(L1)	P2(L2)	P3(L1)	P3(L2)	P4(L1)	P4(L2)
O2	(-0.0245)	(-0.0202)	-0.2042	0.3033	(0.0068)	(0.0599)	-0.5986	0.8550
O3	-0.1249	-0.4625	-0.3950	-0.1643	-0.0828	-0.1016	-0.9849	0.4094
N1	(0.0076)	(0.0059)	(-0.0251)	(-0.1628)	(-0.0631)	(0.1548)	-0.2658	0.0035
Average Distance from Plane								
	-0.1374	0.3839	-0.1079	0.0756	-0.2439	0.3873	-0.2320	0.1380

[a]( ) indicates that the atom was used in the calculation of the least-squares plane.

film measurements were: $a = 9.44(2)\text{Å}$, $b = 12.18(2)\text{Å}$, $c = 18.75(2)\text{Å}$, $\beta = 92.66(9)^\circ$, $\alpha = \gamma = 90^\circ$ and $V = 2156\text{Å}^3$ (25°C, molybdenum radiation, $\lambda = 0.7107\text{Å}$). The complex is isomorphous with and presumed isostructural with the iron complex. The magnetic moment ($\mu_{eff}^{298^\circ K} = 8.97$ B.M.) of an anhydrous sample of the manganese complex has been determined by P. G. Eller (45). The magnetic moment is consistent with that expected (~9.0 B.M.) for a complex with the formulation, $Mn^{II}Mn_2^{III}(SALGLY)_4$.

A second manganese complex was characterized by carbon, hydrogen and nitrogen analysis (ch. II, p. 128). It has been formulated as, $Na_2[Mn(SALGLY)_2]\cdot 3H_2O$, and presumably contains only manganese(II) ions, as evidenced by its light yellow color and its apparent instability in air when wet.

CHAPTER IV

CONCLUSIONS

Prior to this work, several investigators (39, 40, 44) reported the preparation of salicylideneglycinate complexes with first row transition metal ions. Some of these complexes were purported to contain polynuclear units with subnormal magnetic moments. The cobalt complex, in particular, had an unusually low moment of 2.89 B.M. for a cobalt(II) compound tentatively formulated as Co(SALGLY)(GLYCINE). In an effort to understand the source of the low magnetic moment exhibited by the complex, the preparation was repeated and x-ray and magnetic studies were conducted on this compound. The results of these investigations are reported in this work. The structure and magnetism of some iron and manganese complexes of salicylideneglycinate are discussed in relation to the structure and magnetism observed for the cobalt complex.

The x-ray structure determinations and magnetic studies revealed a new type of mixed oxidation state polynuclear compound of the general formulation, $[M(II)(H_2O)_6][M(III)(SALGLY)_2]_2 \cdot 2H_2O$. Compounds of this general formulation were observed for the salicylideneglycinate compounds of cobalt, iron and manganese. The ionic complexes are held together by hydrogen bonding and have no apparent magnetic interactions between metal ions. The general sterochemistry of all the metal ions in the compounds is distorted octahedral. In the cases where the metal is either iron or manganese, infinite chains of metal complexes (namely, $[M(H_2O)_6]^{2+}$ and

$[M(SALGLY)_2]^-$) held together by hydrogen bonds exist in the solid state. In the cobalt complex, hydrogen-bonded trimeric units were observed in the solid state.

Since these mixed-oxidation state metal complexes contain the divalent tridentate $(SALGLY)^{2-}$ ligand, which is structurally similar to the pyridoxal-phosphate Schiff bases used as models for the study of vitamin B_6 reactions (20) and for amine oxidase reactions (30), they suggest that mixed oxidation state metal complexes may be responsible for the catalytic activity of certain metal ions in the model reactions. In fact, Hamilton et al. (30) have postulated that the active catalyst in the pyridoxal-phosphate-dependent amine oxidase reaction is a manganese(III) complex and some results indicated that both divalent and trivalent metal ions participate in the reaction. Interestingly enough, all three of the mixed-oxidation state metal salicylideneglycinate complexes reported in this work also have the trivalent metal ion chelated by the Schiff base. Consequently, this observation provides additional evidence to suggest the formation of trivalent metal ion Schiff base chelates in the amine oxidase reaction.

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